

Environmental Technologies Program

Fiscal year 1994



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-LR-105199-94

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

Environmental Technologies Program

Fiscal year 1994



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-LR-105199-94

Contents

The Environmental Technologies Program _____ 1

Detection and Characterization

Laser Raman Spectroscopy for Waste-Tank Characterization _____ 1

Multianalyte Single-Fiber Optical Sensor _____ 3

Waste-Drum Inspection Using Nondestructive Techniques _____ 5

Electrical Resistance Tomography for Subsurface Imaging _____ 7

Soil and Groundwater Remediation

Dynamic Underground Stripping _____ 9

Microbial Filters for *In Situ* Groundwater Bioremediation _____ 12

Passive Soil-Vapor Extraction _____ 14

OHM: the Ohmic Heating Module _____ 16

Robotics

Robotic Handling and Processing of Mixed Wastes _____ 20

Waste Minimization

Carbon-Aerogel Capacitive Deionization of Water _____ 22

Waste Treatment

Molten-Salt Oxidation of Wastes _____ 25

Mediated Electrochemical Oxidation for Treatment of Mixed Waste _____ 27

UV/H₂O₂ Treatment of Aqueous Mixed Wastes _____ 29

Flowsheet Development, Modeling, and Systems Analysis for
DOE Mixed-Waste Treatment Facilities _____ 31

Technology Integration

Risk and Hazards Analyses of Mixed-Waste Treatment Technologies _____ 33

The California Environmental Enterprise _____ 35

Using High-Performance Computing to Evaluate the
Effectiveness of Aquifer Remediation _____ 37

Modeling Pore-Scale Processes in Porous Media _____ 40

Environmental Technologies Program Publications _____ 43

The Environmental Technologies Program

The Environmental Technologies Program at Lawrence Livermore National Laboratory (LLNL) conducts fundamental and applied research to develop, demonstrate, and commercialize innovative technologies for solving environmental problems. The program supports and works with several sponsors so that related research efforts can be multiplied or leveraged for optimum value. Current program sponsors include:

- Department of Energy Office of Waste Management (EM-30)
- DOE Office of Environmental Restoration (EM-40)
- DOE Office of Technology Development (EM-50)
- U.S. Environmental Protection Agency
- National Aeronautics and Space Administration (NASA)
- Strategic Environmental Research and Development Program (SERDP)
- U.S. Air Force
- U.S. Army Corps of Engineers
- U.S. Navy
- California Environmental Protection Agency

The Environmental Technologies Program conducts a portfolio of research and development activities that apply LLNL capabilities to meet specific environmental needs. This portfolio evolves according to the needs of sponsors and as individual projects are initiated and completed. Strategically chosen niche areas of current focus include *in situ* remediation; alternative waste-management technologies; advanced techniques for data acquisition, site investigation, and remediation process monitoring; and selected analytical and supporting technologies.

The first focus, *in situ* remediation, is developing and testing cost- and time-effective *in situ* alternatives to the conventional methods of pump-and-treat, excavate-and-dispose, and soil-vapor extraction. Individual projects include:

- **Dynamic Underground Stripping** for quickly removing free-product subsurface contaminants.

- ***In Situ* Microbial Filters** for low-cost passive bioremediation of organic contaminants in groundwater.
- **Passive Soil-Vapor Extraction** for removing volatile organic compounds from the vadose zone with no energy required.

The second focus, waste management, involves cost- and time-effective alternatives to conventional waste-treatment processes such as incineration, air stripping, activated-charcoal stripping, exchange resins, and reverse osmosis. Specific technologies include:

- **Molten-Salt Oxidation** as an alternative to incineration for mixed-waste treatment.
- **Optimized UV/H₂O₂** treatment for destroying aqueous-phase organics.
- **Capacitive Deionization** to remove inorganic species from water.
- **Supporting technologies** in waste handling, separation, and treatment.

Advanced techniques for data acquisition, site investigation, and process monitoring include cost-saving automated and custom sensor systems such as:

- **Laser Raman spectroscopy** for tank-waste characterization.
- **Computed tomography** for waste-container characterization.
- **Multianalyte, single-fiber-optic sensors** for chemical concentrations.
- **Underground imaging** for tank-leak detection.

Analytical and supporting technologies include advanced numerical models for process characterization, design, and performance assessment, and the development and application of risk-assessment methods for environmental problems and for new technologies. The California Environmental Enterprise helps facilitate our technology transfer, application, and licensing activities in concert with related functions across the state and national environmental field.

ETP technologies are undergirded by basic research and fundamental expertise in materials and processes; these efforts typically involve interdisciplinary work not usually performed by universities or industry. At the other end of the technology-development life cycle, technologies are licensed for commercial product development and application. Licenses are prepared and implemented on a case-by-case basis according to the nature of the technology, its field of use, and the needs of industry partners.

Targets for near-term program development include integrated systems for expedited remediation of the LLNL site; *in situ* cleanup of nonaqueous-phase liquids; *in situ* metals cleanup; low-cost, high-volume water desalinization; low- or ambient-temperature mixed-waste treatment, and integrated risk assessment. These initiatives aim to provide scientific approaches to lower the costs of environmental management, reduce environmental risks, and solve the right problems.

Intermediate- to long-term strategic directions may include areas as diverse as engineered *in situ* processes, mine-effluent problems, geoceramics, unique defense complex or public lands needs, bioproduction of materials, strategic resource recovery, and environmental aspects of new energy-production methods.

More information about the Environmental Technologies Program, its components, and its goals is available on the World Wide Web at <http://www.llnl.gov> or from:

Dr. Jesse L. Yow, Jr.
Program Leader
Environmental Technologies Program
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550

Phone: (510) 422-3521
Fax: (510) 422-3118
E-mail: yow1@llnl.gov

Laser Raman Spectroscopy for Waste-Tank Characterization

Speeding up remediation safety studies

Benefits

- **Rapid quantitative analysis of important tank-waste constituents**
- **Good chemical resolution of entire surface of tank-waste cores in hot-cell environment**
- **Adaptability to core penetrometer for in-tank characterization**
- **In-tank methods can greatly speed up safety surveys and reduce worker exposure**

Large underground tanks of mixed chemical and high-level radioactive wastes at the Department of Energy site in Hanford, Washington, must be characterized before remediation begins. Current plans are to remove core samples from the tanks to a hot-cell laboratory for analysis, but in-tank characterization would be preferable in many respects. We are developing tools based on Raman spectroscopy for efficient chemical characterization of tank contents. Raman spectroscopy will be used to spatially characterize target species on the surfaces of tank core samples and on salt-cake surfaces in the tanks themselves. A Raman probe in a cone penetrometer will be used to obtain chemical profiles within tank sludges and salt cakes.

A Powerful Tool in Harsh Environments

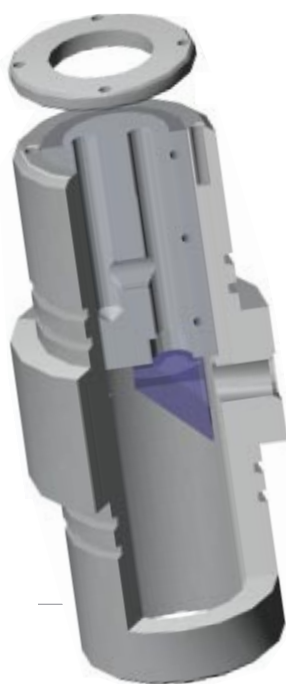
The more than one hundred million gallons of mixed wastes held in 177 underground storage tanks at Hanford are extremely heterogeneous (both chemically and in physical form), and their distribution within the tanks is generally unknown. Before the wastes can be retrieved, treated, and disposed of, safety concerns require that each tank be extensively and quickly characterized to identify the chemical and radioactive composition and the pertinent physical characteristics of the wastes it contains. As part of a joint effort by several national laboratories and universities to address the need for in-tank characterization methods, Lawrence Livermore National Laboratory is to design and deliver spectroscopic tools for chemical characterization. Raman spectroscopy will be one of these tools.

Raman spectroscopy identifies inorganic and organic chemicals by means of their vibrational spectra. Readily available laser light sources in the visible and near-infrared regions can be used advantageously to interrogate samples. Visible and

especially near-infrared light is very efficiently transmitted over long distances by fiber optics, making Raman a powerful tool where it is inconvenient or unsafe for workers to make contact with the sample.

We are collaborating in developing and testing fiber-optic laser Raman techniques for deployment in hot cells and waste tanks at Hanford. Raman spectroscopy can identify many key tank constituents, such as nitrates, nitrites, ferri- and ferrocyanides, and chelating agents. Single-point fiber-optic probes, which interrogate a sample one point at a time, have been successful in identifying key constituents such as nitrates in simulated tank samples.

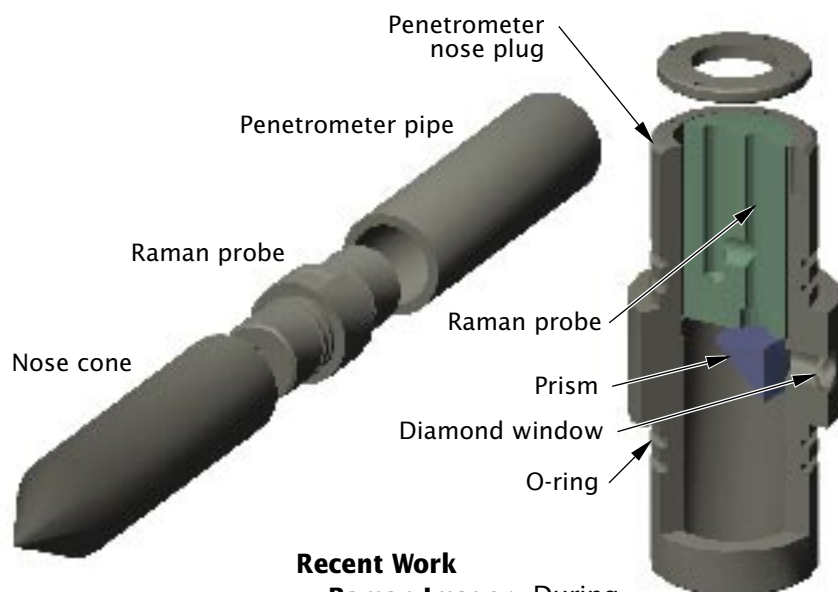
Cone penetrometers offer a faster, safer, and more cost-effective alternative to removing tank core samples for laboratory analysis. A cone penetrometer is being planned for in-tank application at Hanford. Probes suitable for use in penetrometers already exist for characterizing tank waste porosity, density, temperature, and electrical conductivity. Raman probes would provide crucial additional chemical-composition measurements.



Contact:

Kevin Kyle
(510) 423-3693
E-mail: kyle2@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY



The steel Raman probe assembly threads into the nose cone and pipe of a standard cone penetrometer. The probe fits inside the assembly, protected from the penetrometer pressure loading and from the harsh tank waste. A prism establishes an optical path between the Raman probe and the exterior of the penetrometer. Fiber-optic cabling between laser source, Raman probe, and Raman spectrograph is threaded through the penetrometer pipe.

Recent Work

Raman Imager. During 1994 we built a prototype benchtop model of a fiber-optic Raman imager for surface chemical analysis of tank cores. Output from a visible-light argon-ion laser is directed to x, y scanning mirrors that permit the laser beam to be swept into a stripe across the core. This stripe is imaged onto the slit of a monochromator, which is in turn imaged on a charge-coupled-device detector, so that the chemical composition along the entire stripe can be determined. Sweeping the stripe along the core, or moving the core through the stripe, permits rapid surface analysis of the entire length of the core.

At standoff distances of several feet, the prototype imager detected potassium ferrocyanide on the surface of a simulated core at very low concentrations; detection at concentrations of 0.1% by weight should be possible in routine use of a Raman imager designed and built for core sample analysis.

A drawback of standoff imaging at visible wavelengths is its sensitivity to ambient room illumination, particularly to fluorescent (mercury-based) lights, whose strong mercury lines fall at about the same wavelengths as important Raman bands from ferri- and ferrocyanide. We believe that the imager's sensitivity to fluorescent light can be overcome by using near-infrared laser excitation.

The imaging system offers generally better performance than a single-point, contact, fiber-optic Raman probe. The

prototype imager is ten times more sensitive to the ferrocyanide ion than the single-point probe, indicating the importance of a wide field of view for Raman probe design. The single-point probe must be less than a centimeter from the sample surface, so surface irregularities can cause large variations in signal strength. Material from the surface can adhere to the probe tip, obscuring the light path. Unwanted Raman signals arising from the silica glass fibers cannot be conveniently removed from the single-point probe's laser beam before it impinges on the sample; if fiber optics were to be incorporated in an imager designed for hot-cell use, the unwanted glass Raman signal could easily be filtered.

We have developed a conceptual design for a robust fiber-optic Raman probe for the in-tank cone penetrometer. This probe should provide real-time chemical profiles vs depth of tank waste during interrogation with a penetrometer. The design shields the probe from direct contact with harsh tank wastes, protects it against the high force loads that may be required to drive the penetrometer into the waste matrix, and uses materials offering reasonable ability to operate in strong radiation fields. We identified sapphire as a suitable material for key optical components of the probe. We will construct a prototype probe based on this design in 1995.

Other Chemical Sensors Deployable in Waste Tanks. Although Raman spectroscopy can be used to identify many of the important components of tank wastes, it cannot do the whole job. We therefore surveyed other sensor technologies that might be incorporated in the cone penetrometer to give information on pH and on gaseous, liquid, and solid species insensitive to Raman interrogation, such as metal ions and elemental species. We also surveyed sensors that can monitor toxic or explosive gases or vapors.

We identified chemical sensors for hydrogen, ammonia, volatile organic compounds, ferrocyanide, cyanide, cesium-137, strontium-90, technetium, plutonium-239 and -240, and uranium-235 and -238, as well as other sensors for heavy metal ions, nitrate/nitrite ratio, and iron (as an indicator of ferrocyanide).

Multianalyte Single-Fiber Optical Sensor

In situ measurement of multiple chemical substances saves time and expense

Benefits

- Detection of multiple chemical compounds using sensors in a single optical fiber
- Hardiness to environments with high levels of radiation, magnetic flux, or temperature variation
- Many applications in remote and in situ measurement

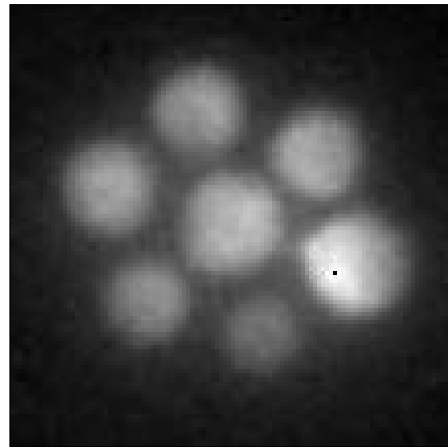
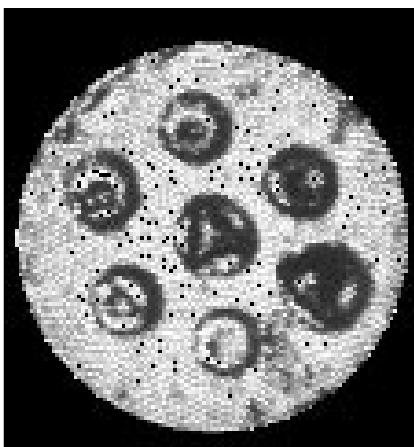
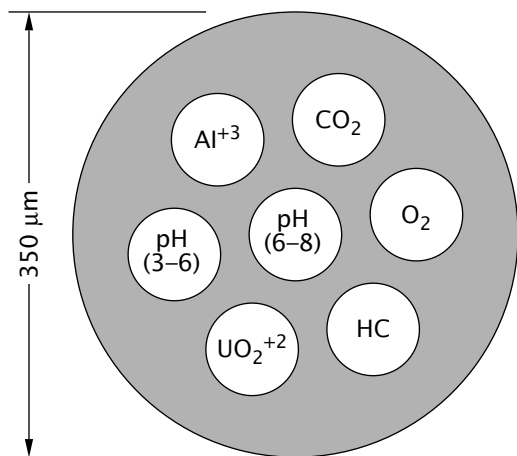
Fiber-optic sensors offer tremendous potential for remote and in situ measurement of contamination. Current methods for detecting nearly all priority contaminants require samples to be collected and submitted for laboratory analysis, which can take up to 30 days to get results. Optical sensors allow in situ measurement of contamination in real time, saving time and expense. However, current sensor technology is limited to single-fiber sensors that can detect single compounds, and many contaminated sites have dozens, if not hundreds, of pollutant compounds present. A unique technology has been developed that enables multiple sensors to be placed in a single optical fiber to measure the concentrations of various chemical constituents.

One Instrument Can Measure Several Compounds

The technology is based on a unique method patented by Tufts University that enables multiple sensors to be placed on the end of a single optical fiber. We are collaborating with Tufts in developing the

technique. As many as 20 different sensors (for different target compounds) can be placed on a single fiber only 350 micrometers in diameter.

Sensing regions are placed at precise locations on the end of an imaging optical fiber, and the signals from each region are



Potential configuration of the multianalyte sensor, with seven sensors for simultaneous determinations of aluminum, carbon dioxide, oxygen, nonspecific hydrocarbons, uranium oxide, and pH in two ranges. The center image is a microphotograph of a successful deposition of

seven individual sensing elements on a single 350-micrometer-diameter imaging fiber. The individual 6-micrometer channels of the imaging fiber are partially visible. At right is an image from a charge-coupled-device detector showing fluorescence signals from the sensors.

Contact:

Fred Milanovich
(510) 422-6838
E-mail: milanovich1@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

monitored simultaneously. The imaging fibers contain several thousand discrete light-transmitting channels that coherently relay an image from one end to the other. The sensors are designed to fluoresce when illuminated by light at a particular excitation wavelength. Each individual sensor changes its fluorescence intensity according to changes in the concentration of a particular chemical substance.

Optical fibers can be used in environments with high levels of radiation, magnetic flux, or temperature variation. The fiber-optic array offers the potential for single rapid or portable multianalyte screening and monitoring of mixed wastes. The unique multiplexing of this sensor allows a single instrument to measure more than one compound to the parts-per-million level.

Recent Work

We have designed and built a portable, low-cost instrument to make useful field measurements using multianalyte fiber sensors. Field tests of this instrument are scheduled for the summer of 1995. The suite of compounds to be measured will be chosen to match the application. Recently, we have been considering a bioremediation application in which oxygen and carbon dioxide sensors would help monitor the life signs of microorganisms. We anticipate that our application-specific technology will be available for field-of-use licensing and have established informal collaborations with several instrument component manufacturers.

Waste-Drum Inspection Using Nondestructive Techniques

Accurate assay will cut disposal costs

Benefits

- Identifies radioactive sources distributed nonuniformly in nonhomogeneous matrices
- Detects lower radioactivity levels than conventional segmented gamma-scanners can
- Certifies when radioactive or mixed wastes are LLW—that is, below the TRU threshold, and quantifies TRU wastes for final disposal

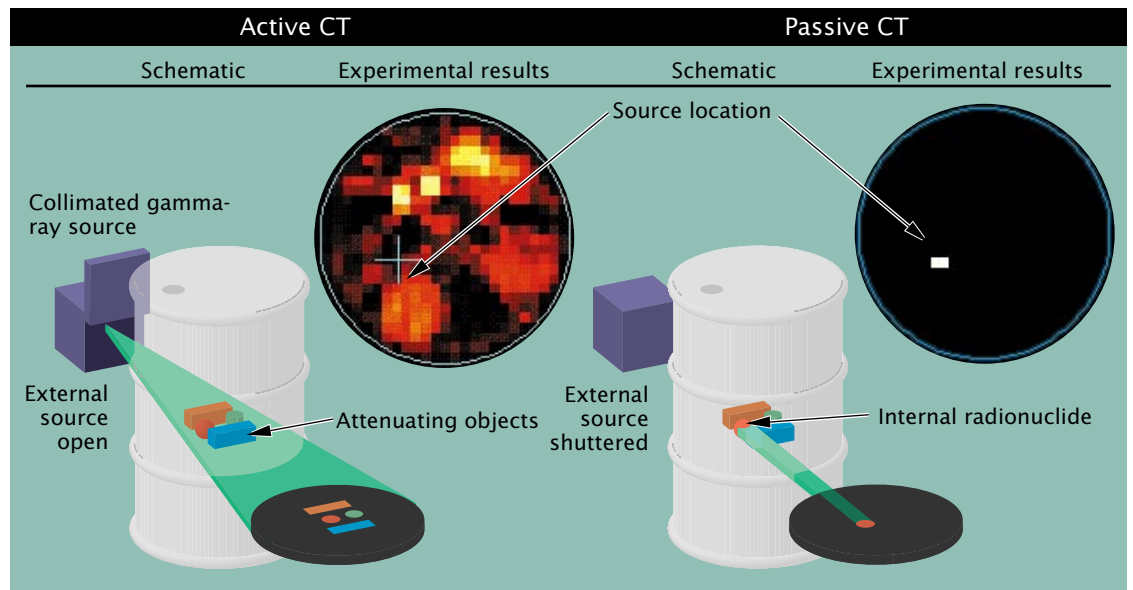
Before drums of mixed waste can be properly stored or disposed of, the contents must be known. Hazardous as well as “nonconforming” materials (such as free liquids and pressurized containers) must be identified, and radioactive sources and strengths must be determined. Opening drums for examination is expensive because of safety precautions. Current nondestructive methods that can characterize waste without requiring drums to be opened are often inaccurate, and cannot identify nonconforming materials. We are developing a combination of nondestructive evaluation and assay (NDE/NDA) techniques that can analyze closed waste drums accurately and quantitatively.

The Most Accurate Technology Available

Regulatory agencies require that all radioactivity in closed waste containers be accurately identified so that the containers can be properly classified for disposition—as low-level waste (LLW) or pure transuranic waste (TRU), for example. Existing nondestructive technology cannot accurately measure the small amounts of radioactivity that determine classifications. For example, in a 55-gallon drum

containing 100 kilograms of wastes, only 160 milligrams of plutonium is necessary to exceed the TRU threshold. Disposal costs for different categories vary significantly. Since most radioactive wastes generated at Department of Energy sites are considered to be TRU wastes until proven to be otherwise, a technology that can accurately differentiate between categories for disposal could save thousands of dollars per drum.

In active and passive computed tomography, active CT quantitatively maps the contents of a drum, passive CT identifies and locates radioactivity, and the active measurement is used to correct the passive radioactive intensities for attenuation caused by drum contents.



Contact:
Harry Martz
(510) 423-4269
E-mail: martz2@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

We have developed a system of active and passive computed tomography (CT), a comprehensive and accurate gamma-ray NDA method, that can identify all detectable radioisotopes present in a container and measure their activity. This may be the only technology able to certify when mixed wastes are below the TRU threshold, determine if they meet regulations for LLW, and quantify TRU wastes for final disposal. Projected minimum detectable levels are expected to be lower than those obtainable with a segmented gamma-ray scanner, the method currently in use throughout the Department of Energy.

Measures Nonuniform Sources in Nonhomogeneous Matrices

Conventional segmented gamma-ray scanners can account for attenuation if the radiation source is uniformly distributed in a homogeneous attenuating matrix. Real waste drums rarely meet either of these conditions. The new active and passive CT (A&PCT) technology can measure nonuniform sources in nonhomogeneous matrices.

The operating principles of the A&PCT technology are simple: (1) the active CT measurement uses gamma rays at different energies to map the unknown waste matrix in a drum, revealing the attenuating objects; (2) the passive CT measurement locates and identifies any radioisotopes present; (3) combination of the two measurements enables us to correct the measured radioactive intensities for attenuation caused by drum contents. These corrected passive intensities provide an accurate quantitative measure of the source strength of all detected internal radionuclides; they enable us to classify detected radioactivities within the drum as transuranic or low-level, in order to meet repository regulations.

Currently the A&PCT system produces two-dimensional images of cross sections of the container contents. We are working with the University of California at San Francisco, School of Medicine, Department of Radiology to develop a three-dimensional image-reconstruction program.

Recent Work

We completed assembly of a full-scale prototype A&PCT scanner for 55-gallon drums in 1993. It contains a three-axis manipulator that elevates and rotates the drum under inspection, and one detector; once the method is proven, it is straightforward to construct a multiscanner detector for more rapid assay. We began test scans of drums of simulated representative waste matrix materials in 1994. Preliminary scans of a drum containing plastic bags of paper, glass, and metal and a radioisotope source were successful.

In another set of experiments, a drum contained well-characterized TRU items packed in the lowest third of the drum, medium-density LLW items in the middle third, and combustible LLW items in the top third. We found excellent agreement between our results and the known calibration assay of radioactive sources used in these complicated attenuating matrices.

Future efforts will focus on developing the three-dimensional reconstruction to allow analysis of radioactive sources of any geometry, optimizing the operating parameters for LLNL's representative wastes, and conducting scans on real LLNL waste drums. We are collaborating with an industrial partner to develop a mobile (truck-based) Waste Inspection System (WIT); the system will be ready to be deployed at selected Department of Energy sites at the end of 1996.

Electrical Resistance Tomography for Subsurface Imaging

Higher resolution at lower cost

Benefits

- Unprecedented subsurface detail (at depths of 10–500 feet)
- Two- and three-dimensional imaging
- 50–75% fewer boreholes than conventional techniques
- Updated survey images in 1–6 hours
- Electrodes are rugged, inexpensive, and easily emplaced
- Effective in both clay-rich and sandy soils

Current methods of subsurface imaging in underground cleanup operations allow only limited one-dimensional resolution. High-resolution imaging is needed to better define site characteristics, monitor remediation activities, and delineate natural processes that control contaminant migration. Electrical resistance tomography (ERT), a new method that produces two- and three-dimensional subsurface images, provides dramatically increased resolution and sensitivity. It also saves on drilling costs and site damage because fewer boreholes are required than in standard borehole logging.

Mapping Between Boreholes

ERT images are generated from measurements of electrical resistance variations in the subsurface. Electrical resistivity changes underground are caused by natural conditions or manmade processes such as salinity, surface water infiltration, underground tank leaks, and steam or electrical heating during soil cleanup. The technique uses conventional measurements in unconventional ways. First, measurements of currents and voltages are made between boreholes, from the surface, or between boreholes and surface. Second, the data are processed by a mathematical algorithm that solves a highly nonlinear inverse problem to produce a map—a tomograph—of the resistivity distribution.

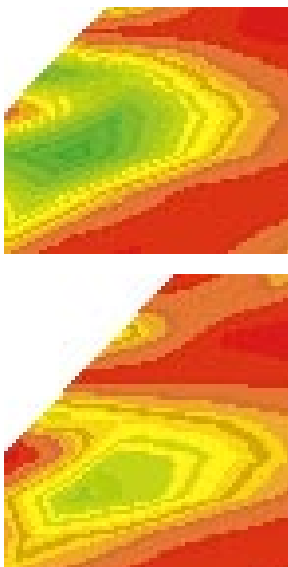
Cross-borehole ERT uses a number of electrodes in contact with the soil in each borehole; it fills in information between boreholes separated by tens of meters or more. Site characterization can be maximized with a minimum of drilling, and high-resolution information is added about fluid flow and other processes important in cleanup and post-closure monitoring activities.

The technique has strong advantages over competing technologies. It provides unprecedented detail of subsurface structures and processes (resolution depends on many factors, but typically is roughly equal to one electrode separation) at depths of 10–500 feet, providing updated survey images in 1–6 hours. Two- and three-dimensional imaging are now possible. ERT cuts costs because it requires 50–75% fewer boreholes than conventional borehole-sampling techniques; the stainless steel electrodes are rugged, inexpensive, and easily emplaced. We have demonstrated the technique in both clay-rich and sandy soils.

Besides site characterization in soil remediation projects, applications of the technique include detection and location of subsurface leaks, evaluation of the effectiveness of cleanup techniques, cleanup process control, and nondestructive evaluation of large structures such as pavements, buildings, and dams.

Recent Work

We are investigating the utility of ERT for detecting leaks from metal underground storage tanks. Several technical challenges need to be solved. The high electrical conductivity of the metal tends



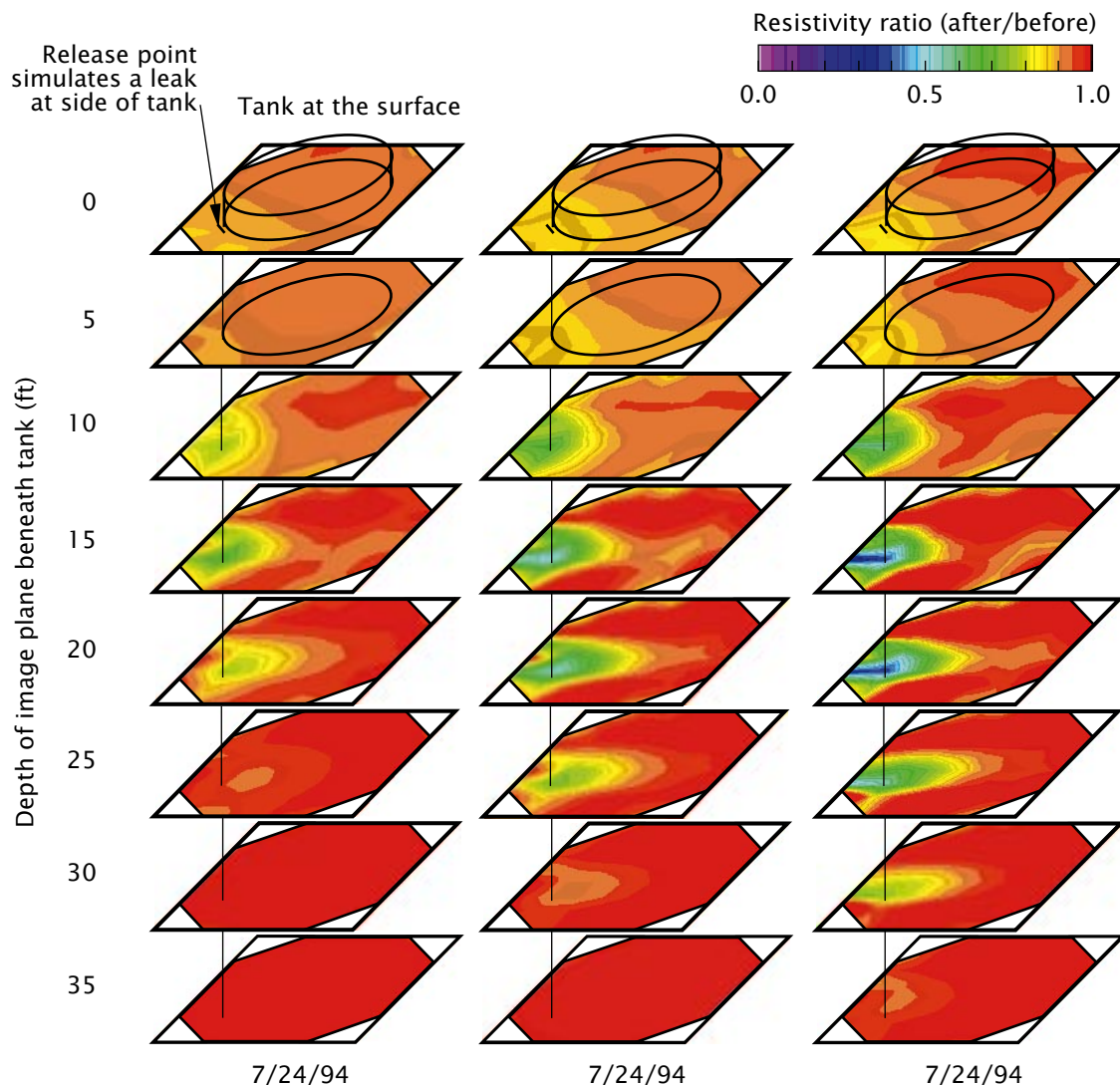
Contact:

Abe Ramirez
(510) 422-6909
E-mail: ramirez3@llnl.gov

Bill Daily
(510) 422-8623
E-mail: daily1@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

ERT images made during a brine release from an underground storage tank. The image planes, when assembled together, give a detailed view of the plume formed beneath the tank during the release.



to short the electrical currents used to probe the subsurface, possibly reducing or eliminating the sensitivity of ERT to these releases.

In the first of two brine-release experiments conducted at Hanford, Washington, in 1994, we used low-concentration test brine that was much harder to detect than real tank brines; ERT successfully detected and located the leak and the spilled volume of brine. In a second experiment, still ongoing, the leak is near the center of the tank and thus harder to detect. Future experiments will evaluate the performance of the technique under more complex conditions such as increased electrical noise and rainwater infiltration.

We are also testing the use of ERT for monitoring and tracer movement during electrokinetic remediation; initial images

made in a test at Sandia National Laboratories showed that the technique was able to map the movement of water being added to the site.

Work for 1995 includes expanding the data-processing algorithms to fully three dimensions (electric current is now analyzed in three dimensions but resistivity is constrained to two). One of the major objectives is to produce a code that is as practical to use as the two-dimensional one—that is, accurate and fast. We will also conduct an experiment to determine if ERT can detect nonaqueous-phase liquids such as trichloroethylene.

We are actively seeking to transfer the technology to commercial partners who can provide the ERT surveys needed at many government and industrial sites.

Dynamic Underground Stripping

60 times as effective as conventional methods of groundwater cleanup

Benefits

- Avoids the long-term investment of conventional methods
- Treats contamination both above and below the water table
- Removes separate-phase (free-product) contaminants
- Is effective in low-permeability soil
- Remediates quickly; reduces risk to population

Underground spills of volatile hydrocarbons (fuels and solvents) are especially difficult to clean up when they are trapped both above and below the water table. Dynamic Underground Stripping is the first technology able to clean up this situation and remove even separate-phase contaminants below the water table. The subsurface is heated above the boiling point of water and then both contaminant and water are removed by vacuum extraction. Field results show that the process is more than 60 times as effective as pump-and-treat to clean contamination below the water table, and 15 times as effective as vacuum extraction above the water table.

Cleanup Below the Water Table

Cleaning up volatile hydrocarbons with conventional techniques has had limited success. The classic method of pump-and-treat takes many years, uses huge amounts of water to remove little contaminant, and is of little use for separate-phase contaminants such as free-product gasoline that have low solubility in water. Vacuum extraction has been very effective at removing highly concentrated contaminants in the vadose zone (above the water table), but neither method is useful below the water table.

Three Integrated Technologies

Dynamic Underground Stripping relies on three integrated technologies.

Steam Injection. Steam is pumped into injection wells, heating the contaminated earth to 100°C. The steam drives contaminated water toward the extraction wells where it is pumped to the surface. When the steam front encounters contamination, volatile organic compounds are distilled from the hot soil and are moved to the steam/groundwater interface, where they condense and are pumped to the surface.

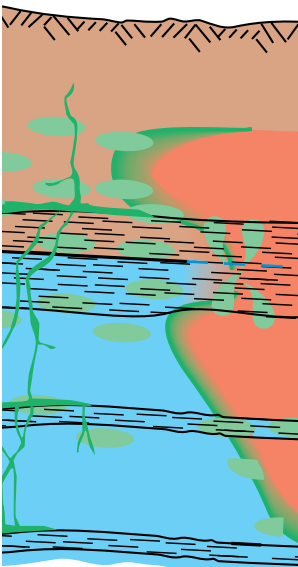
Vacuum extraction continues after full steaming of the contaminated zone to remove residual contaminants.

This technology, developed at the University of California at Berkeley, is well suited to large permeable aquifers that contain separate-phase contaminants.

Electrical Heating. This LLNL-developed technique heats clay and fine-grained sediments and causes water and contaminants trapped within the soils to vaporize and be forced into the steam zones, where vacuum extraction removes them.

Electrical heating is ideally suited for tight, clay-rich soil and near-surface (less than 20 feet) cleanups.

Underground Imaging. To monitor the Dynamic Underground Stripping process, imaging methods are used to map the boundary between the contaminated zone and the cooler surrounding areas. Electrical resistance tomography has proven to be the best technique for obtaining near-real-time images of the heated zones.

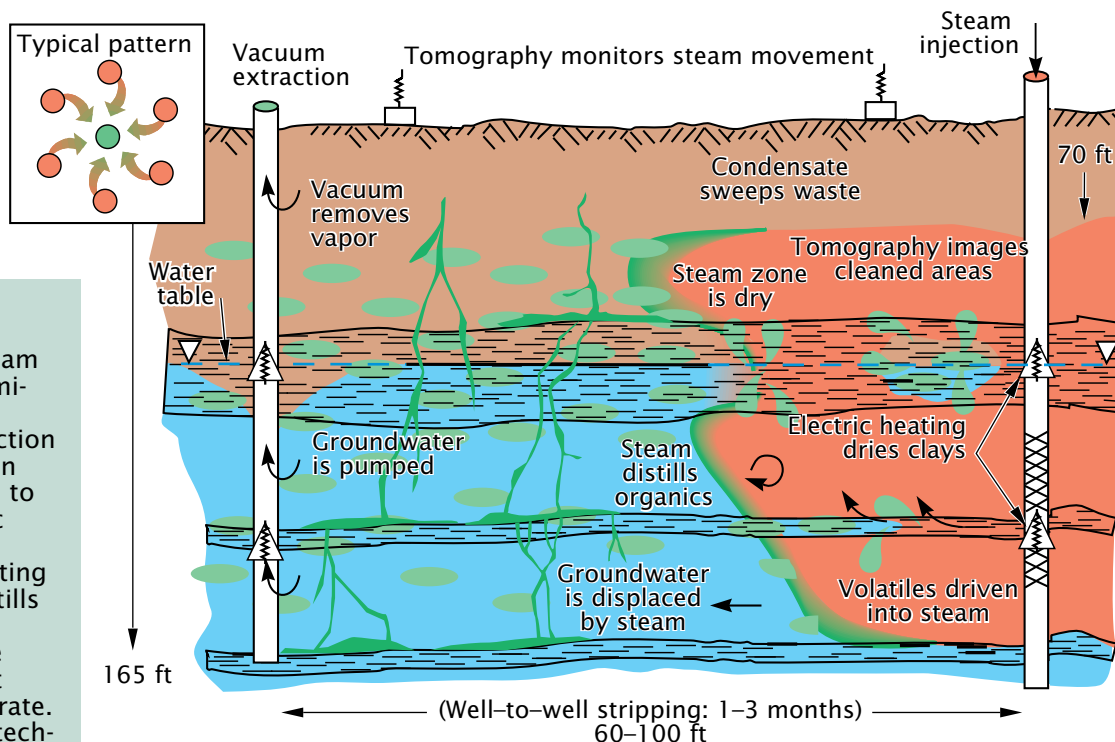


Contact:

Robin Newmark
(510) 423-3644
E-mail: newmark1@llnl.gov

Roger Aines
(510) 423-7184
E-mail: aines1@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY



In Dynamic Underground Stripping, steam drives contaminated water toward extraction wells and then heats the soil to distill organic compounds. Electrical heating dries and distills impermeable clays that the steam cannot readily penetrate. Geophysical techniques monitor the process. The method operates both above and below the water table and is particularly economically attractive for removing separate-phase contaminants (solid green areas).

This LLNL-developed technique is necessary for controlling the thermal process and for monitoring water movement. Tiltmeters provide additional information regarding the shape of the steamed zone.

Successful Full-Scale Test

The first full-scale test of the method, at the site of a gasoline spill at LLNL, was extremely successful. The site had been treated with vacuum extraction since 1988; about 2000 gallons of gasoline had been removed from the vadose zone, but the rate had dropped to only 2 gallons a day by the end of 1991. During 21 weeks of operation in 1993, Dynamic Underground Stripping removed more than 7600 gallons of gasoline trapped in

soil both above and below the water table. Free-product gasoline contamination had extended to more than 120 feet deep.

The maximum removal rate was 250 gallons of gasoline a day. (Pump-and-treat would have removed only about a half gallon a day.) Approximately 100,000 cubic yards were cleaned at a cost of \$60-\$70 a cubic yard.

Recent Work

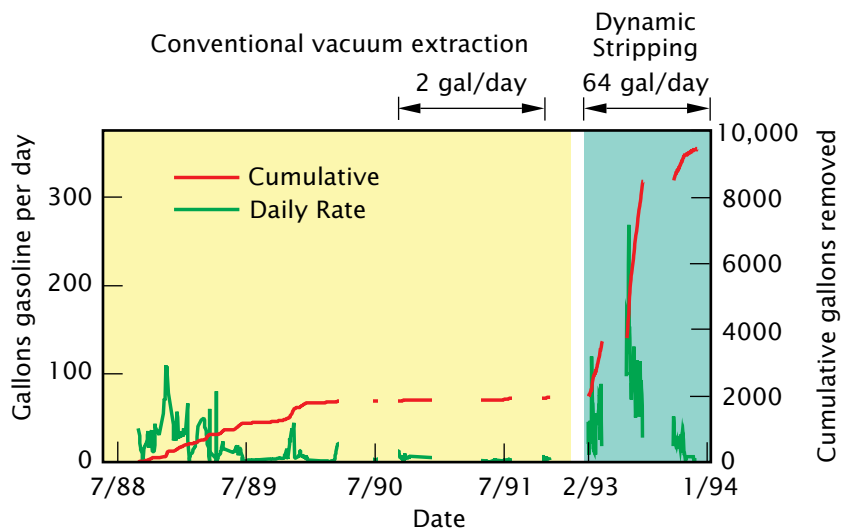
Conclusions from Full-Scale Test. By October 1993, only 750 gallons of gasoline were estimated to be remaining in the clay soil unit at the site. Subsequent activities focused on final cleanup; about 1000 gallons more were removed before the end of the year. After a 1-month shut-down during December 1993-January 1994, groundwater pumping and vapor extraction resumed; extraction rates fell to nearly zero and have remained low.

During the shutdown, gasoline concentrations in the water decreased, and vapor concentrations increased only slightly. Previous shutdowns with hot ground resulted in large increases in concentration when the treatment system was turned on again, presumably due to mobilization/vaporization of free-product gasoline. This and other factors such as the dramatic decrease in groundwater benzene concentrations—from several thousand parts per billion (ppb) before Dynamic Underground Stripping to less than 100 ppb in January 1994—indicate that there is no significant free-product gasoline remaining in the treatment zone.

This goal would have been unattainable by other methods in this time frame or cost range. The cost to remediate the LLNL site in 6 months was \$6–8 million; the estimated cost using pump-and-treat was \$20–60 million over 30–60 years.

Technology Commercialization. We are pursuing commercialization of the technology: negotiations are ongoing with companies interested in licensing and with remediation contractors and suppliers interested in partnering for further technology and market development. Planning is under way for implementation at several contamination sites in 1995. Simultaneously, we will continue to conduct tests on additional fuel spills and on new contaminants and soil or rock types to expand the applicability of the method.

Design to Address Constraints at Pinellas Plant Cleanup. We have produced a preliminary design for applying Dynamic Underground Stripping to groundwater contaminated with volatile organic compounds at the DOE Pinellas Plant in Florida. This site is the pilot project for the DOE Integrated Treatment



Remediation Demonstration Project. Two separate plumes with high levels of methylene chloride extend adjacent to and beneath a pond that is a designated National Wetland; since the pond water is not contaminated, a major concern is that any treatment program used should not affect the pond in any way.

The primary constraints on the design for this site are the proximity to the surface (concern about surface breakthrough), the relatively low soil permeability (long breakthrough times for steam), and the pond (need for precise process control). By using central injection with peripheral extraction, and a thermal and vapor barrier at the surface, the system can maintain maximum process control. Our calculations indicate that Dynamic Underground Stripping may be able to remove even residual contamination and separate-phase hydrocarbons at the site to extremely low levels, with minimal effect on the soil porosity.

Dynamic Underground Stripping removed gasoline contamination above the water table at about 15 times the rate of conventional methods, and groundwater contamination at more than 60 times the conventional rate.

Microbial Filters for *In Situ* Groundwater Bioremediation

A new way to use soil bacteria to degrade contaminants

Benefits

- Cheaper and more permanent cleanup than pump-and-treat provides
- Optimal degradation of target contaminants by specially cultured microbes
- Minimal maintenance
- Remediation of many classes of contaminants

In situ bioremediation of contaminated aquifers promises real advantages over the standard pump-and-treat process, which is costly and time-consuming, especially for volatile organic compounds. In situ bioremediation uses naturally occurring microorganisms to degrade organic contaminants to harmless compounds; the contaminants are destroyed in situ rather than relocated. However, the usual approach to this technique—pumping nutrients into the contaminant plume to stimulate microbes in the soil—has significant problems in the field. Our microbial filter technology takes a new route, showing reliable results for as little as half the cost of pump-and-treat. It also provides a more permanent cleanup because contaminants are eliminated from both the aqueous and the solid subsurface phases.

Revolutionary Concept

Although other efforts at bioremediation have succeeded in increasing underground bacterial populations by injecting nutrients into the ground, they have not achieved effective contaminant destruction. The infusion of nutrients pushes the contaminant away from the microbes. Also, all of the populations already present are stimulated; the ones that proliferate may not be useful for cleanup. Another difficulty is fouling of the injection wells caused by too much growth around the well bore.

The *in situ* microbial filter concept is revolutionary because specific bacteria are injected—without nutrients. The bacteria are in a resting state and don't require nutrients, but are still metabolically active. Adhering to soil particles, they form a mass—a biofilter—around the end of the injection well. The actual geometry of the filter depends on the injection pattern, but in general a thin region is formed that extends across the expanding contaminant plume. As the contaminant is transported through the filter by groundwater flow, enzymes within the bacteria break it down into harmless compounds, and the

water exits clean. If the natural flow rate is too slow, pumping can bring the water through the filter zone.

Trichloroethylene-Degrading Microbes

Our work focuses on cleanup of chlorinated ethenes such as trichloroethylene (TCE); these volatile organic compounds are a serious source of contamination at many industrial and government sites. The concept can be generalized, however, and can be applied to bioremediation of many classes of contaminants.

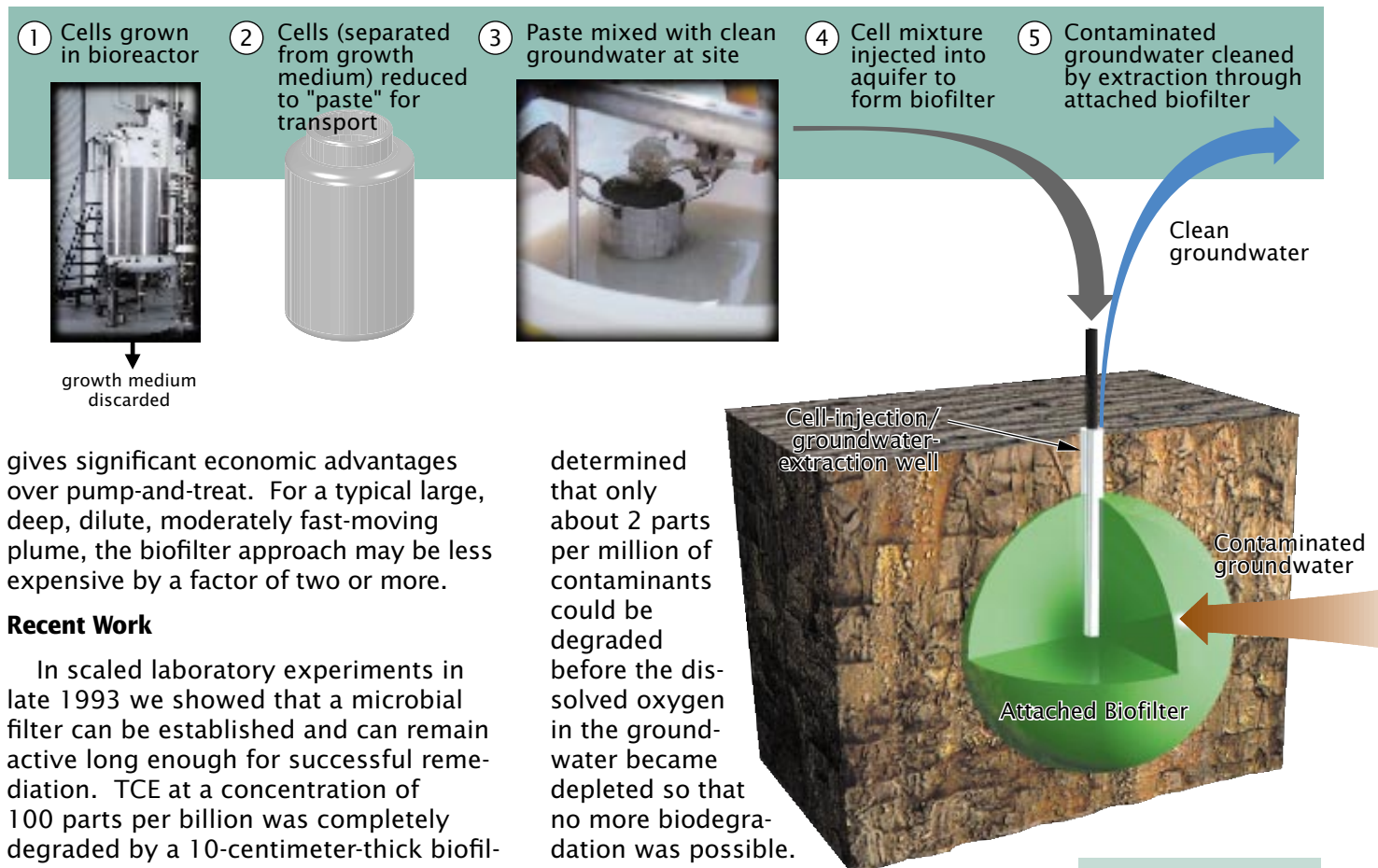
We use naturally occurring harmless soil bacteria, *Methylosinus trichosporium* OB3b, that consume methane. The enzymes they contain to oxidize methane can break down other compounds as well; TCE is broken down into harmless products such as carbon dioxide and water.

One of our breakthroughs is our discovery of a way to culture these microbes so they will continue the catalysis for weeks instead of hours or days. We expect them to function for at least a month in the field before a fresh injection is needed to replenish the filter. No other activity—except monitoring—needs to be conducted between replenishments. This

Contact:

Richard Knapp
(510) 423-3328
E-mail: knapp4@llnl.gov

Ken Jackson
(510) 422-6053
E-mail: jackson8@llnl.gov



gives significant economic advantages over pump-and-treat. For a typical large, deep, dilute, moderately fast-moving plume, the biofilter approach may be less expensive by a factor of two or more.

Recent Work

In scaled laboratory experiments in late 1993 we showed that a microbial filter can be established and can remain active long enough for successful remediation. TCE at a concentration of 100 parts per billion was completely degraded by a 10-centimeter-thick biofilter in less than 60 hours.

Commercialization of bioprocesses like this, however, is held back by the lack of pilot-scale tests and of the large quantities (kilograms) of bacteria that are required. In 1994 we made a major advance in the quantity problem and performed feasibility studies in preparation for field trials.

Large-Scale Cell Production. We developed a unique bioreactor growth facility at LLNL and achieved the first large-scale production of bacterial cells (in this case, *M. trichosporium OB3b*). Production was flawless; the yield was about 3 kilograms of cells, which is sufficient for pilot-scale field tests of the microbial filter technology. The contaminant-degrading characteristics of the cells were proven to meet our performance specifications.

Site Studies for Field Trials. In a joint DOE/NASA project, we assessed the suitability of a small contaminant plume at the Kennedy Space Center in Florida for field tests. Using a downhole tool specially designed at LLNL for measuring the potential degree of biodegradation, we

determined that only about 2 parts per million of contaminants could be degraded before the dissolved oxygen in the groundwater became depleted so that no more biodegradation was possible.

The site was deemed not suitable for further tests because of its inadequate dissolved oxygen.

We conducted field and laboratory tests of a TCE plume at the Chico Municipal Airport in California and found the soil, aqueous chemistry, and contaminant all acceptable. The first field tests of the microbial filter, designed to demonstrate that it can be established and maintained *in situ*, will begin there in January 1995. Our design calls for a line of alternating injection and withdrawal wells perpendicular to the groundwater flow so that the biofilter will intercept the plume and prevent further migration. Monitoring wells placed upstream and downstream of the biofilter will measure its performance.

All regulatory requirements have been satisfied and the California Department of Toxic Substance Control (the lead regulatory agency at the site) has approved the tests. Two industrial partners are providing financial and engineering support.

Steps in establishing an *in situ* microbial filter for cleaning contaminated groundwater. One injection/extraction well is shown. Typically, a line of alternating injection and extraction wells would be used to extend the biofilter across an expanding plume. When natural flow is sufficient to bring the groundwater through the filter, no extraction is needed.

Passive Soil-Vapor Extraction

Using natural soil “breathing” to extract contaminants cheaply

Benefits

- Effective for final cleanup after conventional active VOC-extraction technologies reach inefficiency
- Better than conventional technologies for use at the margins of plumes
- Much lower capital investment, maintenance, and cost of operations
- Works for any contaminant vapor in the vadose zone
- Technology is in an advanced stage of development

Passive Soil-Vapor Extraction (PSVE) is a method for removing underground contaminants by enhancing the natural soil “breathing” that occurs when the atmospheric pressure changes. Small pressure fluctuations increase the penetration of fresh air into the soil, creating a flow of contaminant-laden air to the surface. The process is a low-cost complement to conventional active-extraction methods; investment and maintenance are low and no power is needed. It is also better suited than conventional methods for certain problems in cleaning up volatile organic compounds (VOCs), such as for margins of plumes and for removing residual contaminants after active-extraction methods have become inefficient.

Controlled Flow Pathways

The concept is relatively new. Recent improvements in subsurface pressure monitoring (at depths to 60 meters) have revealed that atmospheric pressure changes as small as one millibar are transmitted to that depth and that they cause bulk advection of air through macropores in the soil vadose zone (above the water table). Even the diurnal changes of surface heating and cooling create pressure changes that cause air exchange through the vadose zone. The key to PSVE is to manipulate these natural forces to remediate contaminated areas by using knowledge of the pressure relations between the surface and the subsurface at a given site.

This knowledge can be used to accurately install pathways, such as wells and pipe collection networks, to achieve optimum flow. The flow through these

pathways can then be controlled by solar-powered microprocessor-operated valving systems or solar-powered pumping systems. The PSVE Working Group, formed of experts from six Department of Energy organizations, the Environmental Protection Agency, and private industry, has developed two types of PSVE: wellhead and surface.

In wellhead PSVE, air flow results when the surface and subsurface zones are connected by a well. Controls include (1) one-way valves that allow air to escape from the well but force fresh air to sweep through the soil and exit through the well, (2) monitors to determine the contaminant concentration in the escape air, and (3) a stripper or absorber to remove contaminants from the escaping air stream.

If there is no well present, the air cycles in and out through the soil surface. In surface PSVE the surface is modified to control the air entry by paving,

Contact:

Joseph Shinn (PSVE Working Group Coordinator)
(510) 422-6806
E-mail: shinn1@llnl.gov

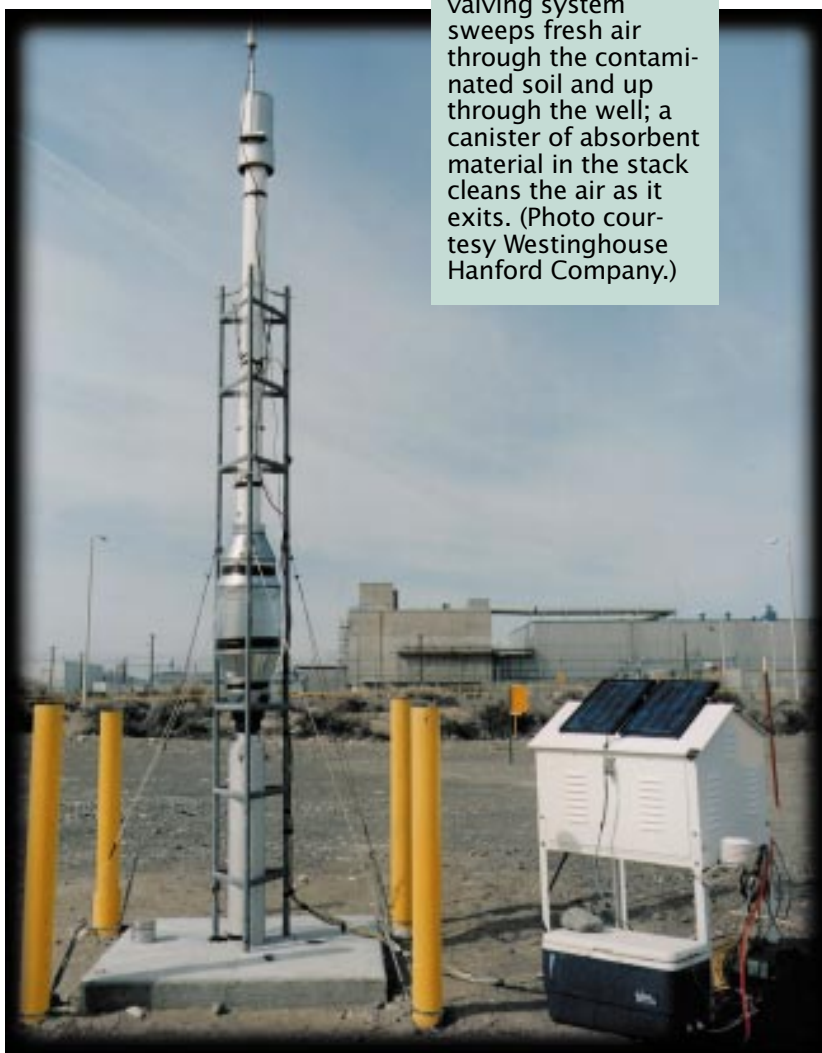
tiling, or similar barriers. Combining these surface modifications with collection pipe networks can cause contaminated air to move laterally to a collection point for stripping, similar to the well-head systems.

Recent Work

Demonstrations have been under way since 1993 at three DOE facilities representing different site conditions: Hanford, Washington; Idaho National Engineering Laboratory; and Savannah River Plant, South Carolina. We are studying the dynamics of the process to optimize removal rate, to minimize plume dispersion, and to exploit the geology and geometry of each situation. Other related technology developments are plume control, off-gas treatment, and active extraction and bioremediation.

The rapid progress of these demonstrations has led us to begin efforts for commercialization. We realized in 1994 that a gap exists between the achievements of the individual demonstrations and the requirements of commercial interests to accept the technology, to contribute commercial investment, and to pursue remediation ventures using the technology. We planned tasks for 1995 that will address the following significant hurdles to commercialization: verify the technology, inform stakeholders of the technology, explore licensing options, locate commercial partners, conduct a market survey, develop a market plan, and provide commercial partners with the knowledge to operate PSVE systems.

Wellhead PSVE system currently being demonstrated at Hanford Area 200 West, Washington. The solar-powered valving system sweeps fresh air through the contaminated soil and up through the well; a canister of absorbent material in the stack cleans the air as it exits. (Photo courtesy Westinghouse Hanford Company.)



OHM: the Ohmic Heating Module

Simulating electrical heating of soil and groundwater to improve thermal remediation technologies

Benefits

- Simulates the effects of electrical remediation technologies
- Can be combined with NUFT to model complex, mutually dependent processes
- Allows us to optimize the timing of ohmic heating, steam injection, and vapor extraction

Thermal techniques for in situ groundwater and soil remediation use heat to eliminate water and soil contamination. Heating an underground region either mobilizes contaminants by vaporizing them, modifies them into a harmless chemical state, or entraps them by soil vitrification. However, often there is no adequate means of getting heat from the outside to the center of a zone targeted for cleanup because of low permeability. An alternative approach is to heat the targeted layer internally by passing an electric current through it. To evaluate the effectiveness of this electrical approach to thermal remediation, we developed a three-dimensional computer model of how electrical heating of the soil affects groundwater flow and transport.

Thermal Remediation Techniques

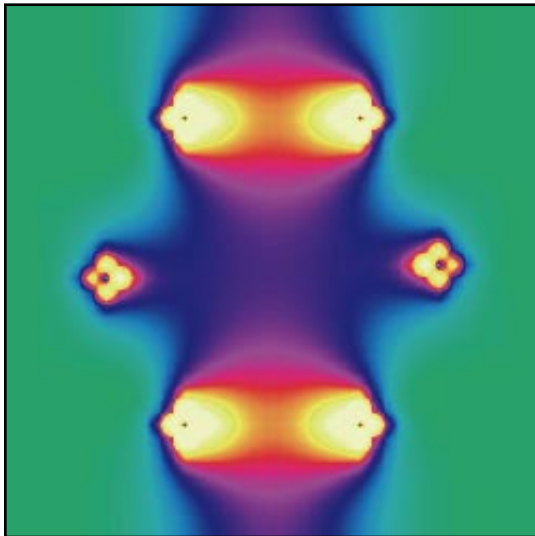
One thermal technique commonly used for remediation is steam injection and extraction. Two wells are drilled on opposite edges of the underground region that is targeted for cleanup. Steam is injected through the first well, called the injection well, into the unsaturated zone. The steam heats the soil and groundwater as it flows through the formation toward the second (extraction) well. This heating creates a steam-plus-condensate mixture that carries the mobilized contaminants to the extraction well, where they are removed.

In this approach, the targeted zone between the injection and extraction wells must be highly permeable, and the contamination must be accessible through these high-permeability pathways. If low-permeability clay layers or lenses are also present and they are a source of trapped contamination, then the steam injection and extraction process may clean merely part of a site

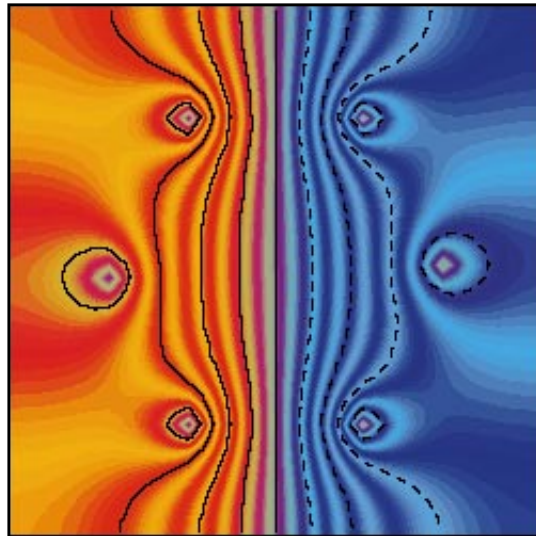
by sweeping contamination from only the highest-permeability pathways. This approach may be adequate for a short time to meet water quality standards, but eventually, contaminants in the larger, unremediated zones of low permeability will leach back into the groundwater and recontaminate it.

A practical method for such problem areas is electrical resistance, or ohmic, heating of the soil and groundwater. Heat can be applied directly to zones that are not accessible to steam and to those that are too large to be heated adequately by thermal conduction alone. Resistance heating of low-permeability layers and lenses produces vaporization, thus enhancing the mobility of the contaminant phase or, at least, increasing the partitioning of a liquid-state contaminant into an existing mobile air or gas phase. The resulting higher pressure of the resistively heated low-permeability zone then drives the vapor-state contaminants into the higher-permeability regions, which can be swept with steam heating.

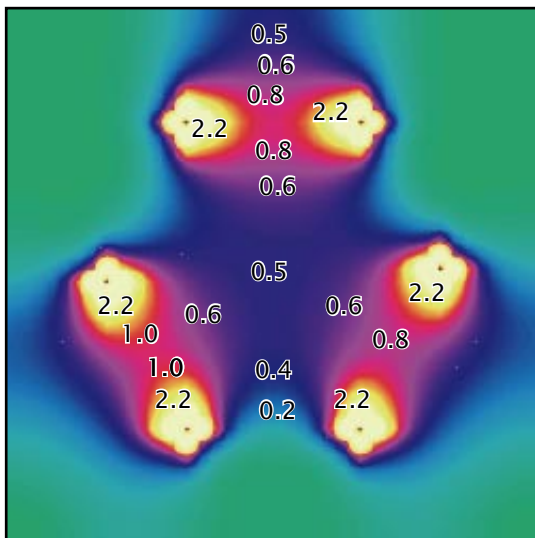
Single-phase model



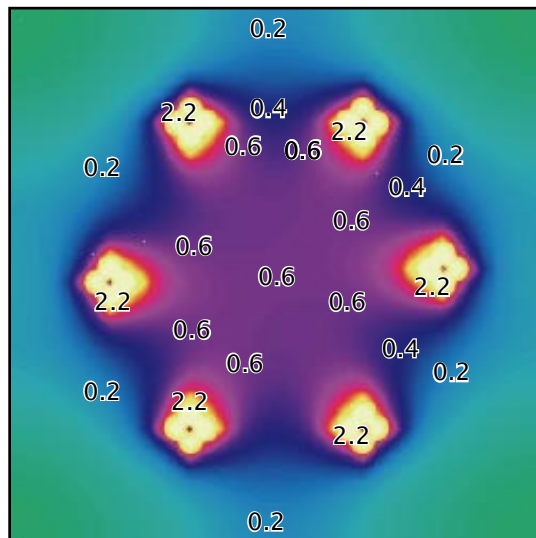
Single-phase electrical-field model



Three-phase model



Six-phase model



By simulating different electrode placements and different phase shifts in the alternating current applied in underground thermal remediation, we can determine how such changes will affect the uniformity of the heating in the zone targeted for cleanup. Here, OHM was used to model six-electrode arrays in uniform media. The spatial uniformity of the initial dissipation rates improves by increasing the number of electrical phases. However, three-phase heating can be made nearly as uniform as six-phase heating simply by periodically regrouping the electrode pairs.

Electrical resistance heating has been combined with steam injection and extraction to heat regions of low permeability that are adjacent to regions of higher permeability. However, in complex hydrogeologic regimes, we must optimize the timing of the ohmic heating, steam

injection, and vapor-extraction operations and thus need numerical models so we can analyze the treatment. We developed a generalized numerical three-dimensional model of the *in situ* ohmic heating process, called OHM, and coupled it to an existing three-dimensional simulator,

called NUFT, that is used to model non-isothermal porous flow and transport. The resulting model allows us to simulate ohmic heat production and transport in hydrologic media of varying complexity.

Electrical System Design: Using OHM in Standalone Mode

The ohmic heating program is modular and may be executed with NUFT or by itself. In standalone operation, OHM can help us understand how electrode placement affects the current flow and, hence, the volumetric heating rate in a volume with a prescribed distribution of electrical conductivity. This approach may be preferred during the initial planning phases of a heating and extraction facility, before detailed hydrologic, geologic, and electrochemical information is added. The module estimates the voltage and current demands on the power supply, the localization of ohmic heating around electrodes, and the effect on joule heating caused by changing electrode placement in either the horizontal or vertical coordinates.

Such calculations are useful for predicting the uniformity of heating in the target formation prior to the heating-induced changes in saturation, temperature, and electrical conductivity. This

modeling provides an approximation to the distribution of dissipative heating, which is useful in designing an electrode array. We also can use it to determine the best electrode configuration for maximizing the heating rate in selected parts of the targeted zone. An important feature of OHM is that it simulates either single-phase or multiphase electrical power to the electrodes, which influences the uniformity of heating and must be considered in designing an electrical system and estimating the associated costs.

Studying Complex Processes: Combining OHM with NUFT

We can also combine OHM interactively with the NUFT hydrologic program to provide a unique tool for studying a variety of complex, mutually dependent processes that must be adequately characterized and understood if electrical remediation is to be successful. For example, the injection of steam at a well can affect the electrical conductivity of the target region because it changes both the saturation and the temperature of the soil. Another thermal effect important for the electrical heating process is the formation of a high-resistivity zone around the electrodes because of the intense heating that dries out the nearby soil. Such a zone, or skin, of high electrical resistivity around the electrodes tends to redistribute the heat dissipation so that

even more heating occurs locally near the electrodes rather than uniformly throughout the soil of the target region. Another concern during the operations stage is the schedule for injecting steam and for ohmic heating. Because large amounts of energy are expended to heat the soil during the stripping operation, we must determine the most cost-effective schedule of stripping and heating for each site.

Recent Work

We are testing OHM in simulations of an electrically heated, partially saturated, porous regime. Our single-, three- and six-phase models of six-electrode arrays in uniform media illustrate the advantages of increasing the number of phases that drive an electrode array. The spatial uniformity of initial dissipation rates improves by increasing the number of electrical phases powering the electrodes sequentially. However, three-phase heating can be made nearly as uniform as six-phase heating simply by periodically regrouping the electrode pairs. Heating uniformity need not be achieved over each power cycle (1/60 second), as is the case for six-phase heating, because the remediation

processes take weeks to months, giving us ample time to make adjustments in the soil-heating distribution. We found that a far more serious problem is the formation of hot spots around the electrodes, which represent a significant departure from heating uniformity.

To simulate hot-spot development near the electrodes, we coupled OHM to the NUFT flow and transport program. These simulations yield a far more meaningful picture of the effect of heating than when we use the OHM module alone.

Preliminary simulations with a fully coupled OHM/NUFT model predict that dry-out around electrodes is a major concern, a prognosis that is also supported by field experiments here. At power levels comparable to those used in the field (200–300 volts), the OHM/NUFT model predicts that a zone of growing desaturation forms around the electrodes. Once drying has severely decreased the flow of electrical current, further heating of the target formation is controlled by resaturation and condensation processes in the dried-out zones. As a result of the model's predictions, we are developing several methods to reduce or eliminate the dryout process in tight clay layers.

Robotic Handling and Processing of Mixed Wastes

Faster, safer, cheaper

Benefits

- **Less personnel exposure to radioactive and hazardous materials and to objects capable of cutting or otherwise injuring human operators**
- **Improved performance of critical tasks**
- **Lower operation costs**
- **Reduced waste generation**
- **Likely applicability at multiple Department of Energy sites**
- **Improved ability to meet key dates under Federal Facilities Compliance Agreement**
- **Consistent with Department of Energy ALARA policies**

In our Mixed Waste Robotics operations we are developing automated systems for handling and processing wastes from the Department of Energy weapons complex, including wastes from underground storage tanks, buried wastes, stored wastes and residues, and materials recovered during decontamination and decommissioning of weapons facilities. Such unknown and potentially dangerous objects and materials must currently be handled in containment systems (ranging in size from glove boxes to room-size systems) or—where such systems are impractical—by human operators dressed in fully encapsulated suits. This generally exposes the operator to ionizing radiation, even with shielding and protective clothing, and to possible accidents caused by unknown hazards.

Automated Handling, Separation, and Analysis of Mixed Wastes

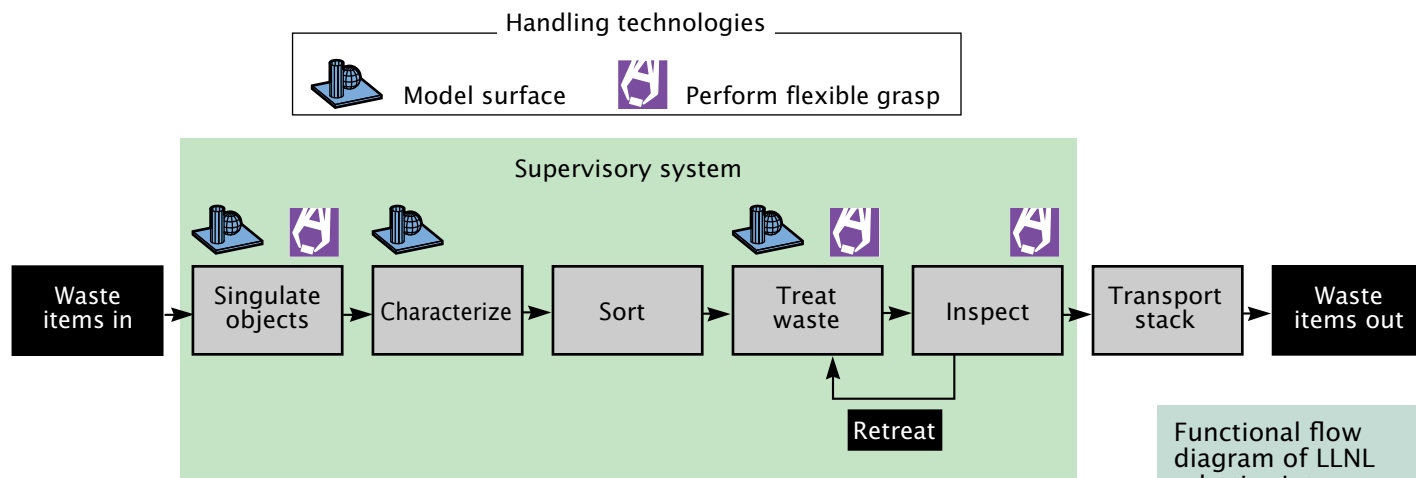
Automated processing of mixed wastes calls for sophisticated technology with multiple capabilities. We have demonstrated automation and robotics hardware and software capable of carrying out three major tasks associated with mixed waste operations.

Singulation. The removal of a single item of waste from a container or from a pile of objects is called singulation. Singulation is a difficult and necessary first step in the characterization and processing of waste items. We have accomplished singulation both as an autonomous robotic task (without the intervention of a human operator) and (for more complex situations) as a vision-based, teleoperated task, in which a human operator is in control of the robot's operations ("human in the loop"). This has required the design and construction of devices suitable for safely and securely gripping objects of a wide variety of shapes, sizes, and weights,

and the development of software capable of determining the shape of an object and of "planning" how to grasp that object to manipulate it.

Characterization and Sorting. We have developed autonomous techniques for characterizing the nature of mixed-waste objects once they have been singulated. This is a difficult second step in the process; waste objects can be homogeneous or inhomogeneous and with greatly differing characteristics. Characterization is needed again in the final stages for inspection to confirm the results of the treatment process. Characterization involves nondestructively and noninvasively determining the weight, structure, radioactivity, and chemical or other toxicity of the object, and localizing the radioactivity and toxicity, if any. Our characterization tools include radiography, computed tomography, gamma-ray spectroscopy, x-ray fluorescence, and eddy-current metal detection.

We have demonstrated the ability to separate metals from nonmetals and to identify homogeneous solid objects suitable for surface decontamination. We have used computer-aided tomography,



Functional flow diagram of LLNL robotics integration demonstration, showing the operations carried out on surrogate mixed-waste samples and the control and material-handling technologies required.

based on gamma-ray scans, to identify the elements of heterogeneous waste items. We have also demonstrated the ability to characterize the contents of intact waste drums.

Waste-Processing Operations. We have developed an automated system for handling and treating noncombustible mixed waste. As one key part of this process, we have demonstrated an automated system that can handle and decontaminate lead bricks, a prominent constituent of the anticipated stream of mixed waste for which inadequate treatment measures existed. We have demonstrated a teleoperated system for cleaning objects of more complex shapes. A commercial frozen-carbon-dioxide cleaning system was integrated into these demonstrations as the treatment method.

Recent Work

We demonstrated the integrated operation of our singulation, characterization, and processing technologies in 1994. Unknown objects representing typical mixed waste were segregated, characterized, treated, and inspected in autonomous mode; all these operations can be taken over by a human in the loop for added flexibility and reliability,

depending on the complexity of the task. Simpler, repetitive tasks can be carried out autonomously.

The integration of all these tasks, the data transfer required, and the overall control of the processes represent major steps forward in the application of robots to complex tasks such as those involved in mixed-waste operations. These capabilities will be used in the Mixed-Waste Management Facility here at Lawrence Livermore National Laboratory (LLNL), for which the Title 1 design is now being prepared.

LLNL is working with a commercial robot supplier on an upgraded glovebox-hardened robotics system whose increased weight-handling ability and improved teleoperation control capability will allow it to be used for characterization, decontamination, and repackaging of tritium-contaminated waste from LLNL's decommissioned Tritium Facility.

Carbon-Aerogel Capacitive Deionization of Water

An efficient, economical process for purifying water

Benefits

- Uses much less energy than competing technologies
- Regeneration without acids, bases, or salt solutions
- Excellent stability in harsh chemical conditions
- The technology has been patented, demonstrated, and automated

The new carbon aerogels, which have very high specific surface area (600–1000 square meters per gram of aerogel) and excellent stability in harsh chemical conditions, make robust and compact water-purifying systems feasible. Capacitive deionization (CDI) using carbon-aerogel electrodes is an efficient and economical new process for removing salt and impurities from water. Carbon-aerogel CDI can be applied to wastewater treatment, water purification, water softening, and desalination.

Improvements Over Conventional Technologies

Carbon-aerogel CDI offers several advantages over conventional water-purification methods. The system has a simple, modular, plate-and-frame construction. CDI uses simple electrostatic regeneration; in ion-exchange systems, regeneration requires acids, bases, or salt solutions. CDI does not require the use of membranes or high-pressure pumps, and the equipment can be much more resistant to the effects of corrosive liquids (used to remove scale) than that used in other methods. And CDI is more energy-efficient than competing technologies—far more efficient than thermal processes.

In carbon-aerogel CDI, the water is passed between carbon-aerogel electrodes that are kept at a potential difference of about a volt; nonreducible and nonoxidizable ions are removed by the imposed electrostatic field and are held at the electrode surfaces, leaving the water pure. When the electrodes become saturated with these salts, they are electrostatically “regenerated,” releasing the salts into a concentrated purge stream.

Some of the energy used in ion removal can be recovered during regeneration, improving overall energy efficiency. Carbon aerogels (developed at

LLNL) are now in commercial production, and their cost should drop considerably as their use in this and other applications increases.

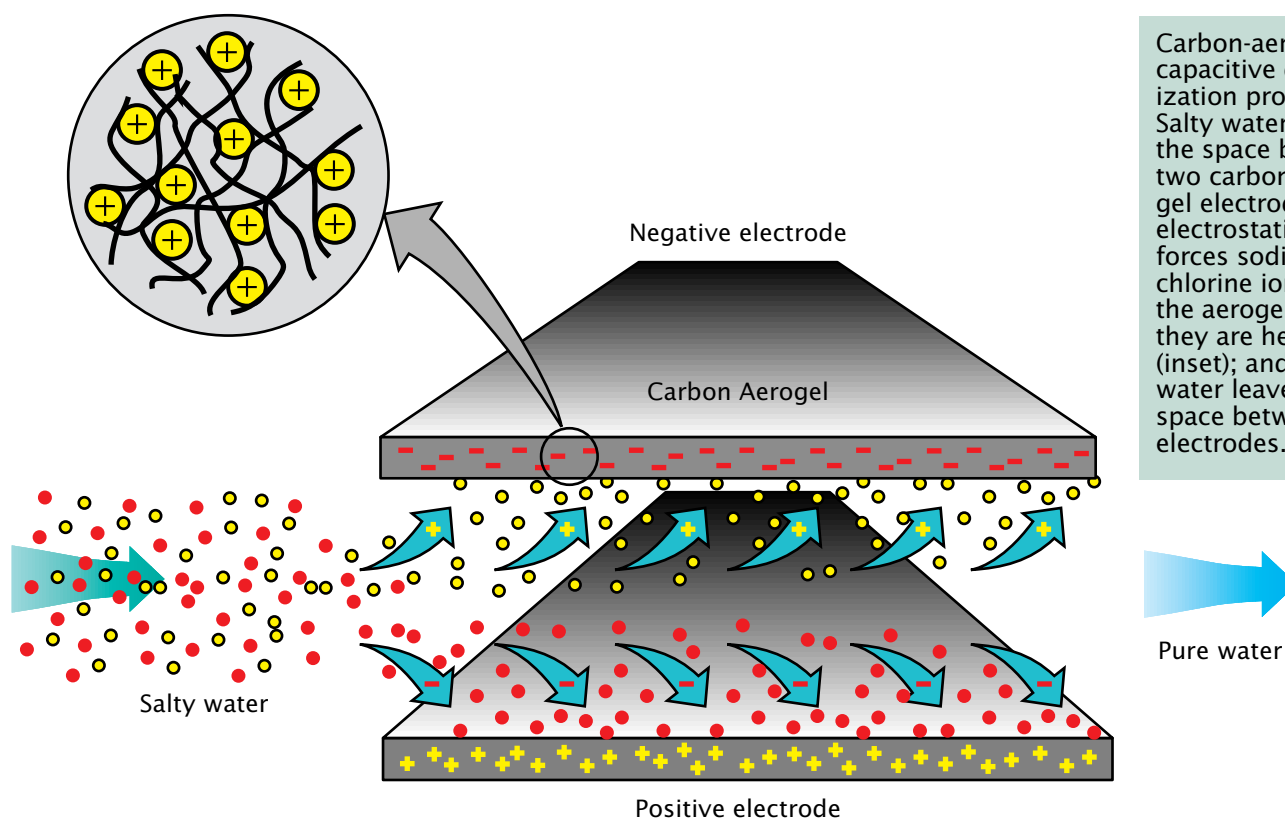
Simple Construction. The carbon-aerogel CDI system uses simple two-sided electrodes, constructed by attaching thin sheets of carbon aerogel to a titanium plate with conducting epoxy cement. (Each square of carbon aerogel is 7 centimeters on a side and 0.0127 centimeter thick; the surface area within each sheet is almost three million square centimeters.) The electrodes are stacked on threaded rods using gaskets and spacers. Slots along one side of the electrode admit water to the gap between adjacent electrodes; the orifices in successive electrodes are staggered, so that water follows a serpentine path through the stack. With the addition of stainless steel headers at the top and bottom, such a stack becomes a complete CDI cell. Our demonstration system has 8 such cells, containing 384 pairs of carbon-aerogel electrodes with a total surface area of over two billion square centimeters (about 54 acres); the system occupies only a few cubic feet of space.

Energy Efficiency. Brackish water (with salt content of 800–3200 parts per million [ppm]) is conventionally purified

Contact:

Joseph Farmer
(510) 423-6574
Mail code: L-369
E-mail: farmer4@llnl.gov

Carbon-aerogel capacitive deionization process. Salty water enters the space between two carbon-aerogel electrodes; the electrostatic field forces sodium and chlorine ions into the aerogel, where they are held (inset); and pure water leaves the space between the electrodes.



using electrodialysis or reverse osmosis. Carbon-aerogel CDI uses 10–20 times less energy per gallon of purified water to accomplish the same results. Purification of brackish water is an extremely important potential application of this technology.

For purifying seawater (32,000 ppm salt), carbon-aerogel CDI is just as energy-efficient as reverse osmosis. It is 10–20 times more energy-efficient in this application than thermal processes such as multiple-effect distillation.

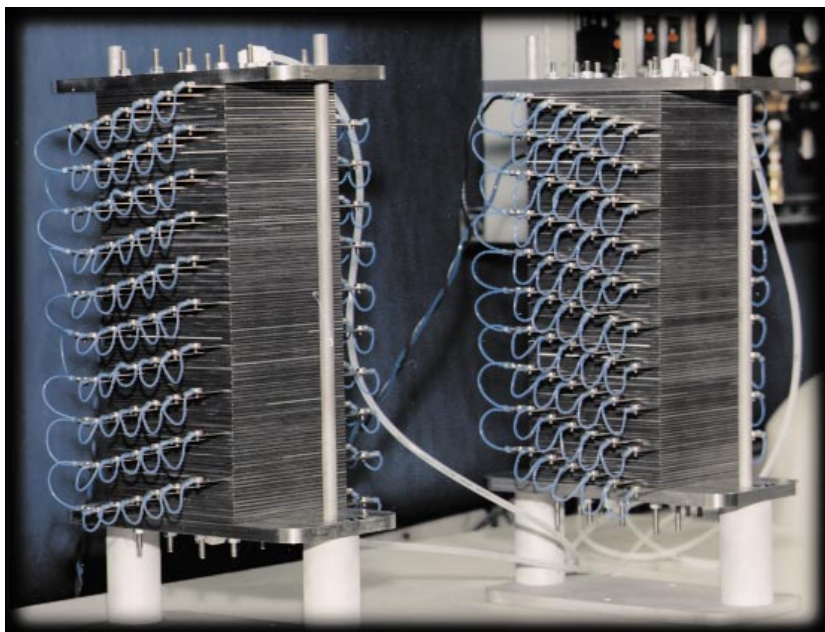
Elimination of Membranes. Carbon-aerogel CDI eliminates the costly and troublesome membranes used in electrodialysis and reverse osmosis. Carbon-aerogel electrodes are chemically resistant; polymeric membranes are attacked by the chemicals used to treat water and remove deposits.

Elimination of Chemical-Regeneration Wastes. Chemical regeneration is required in ion exchange, commonly used for softening household water, treating hazardous and radioactive wastes, treating rinse water from electro-

plating operations, deionizing boiler water for steam and electrical power generation, and producing ultrapure water for manufacturing. Home water softening uses 120–190 pounds of salt per month; industrial applications use 100 pounds of acids or bases to regenerate one pound of ion-exchange resin. The electrostatic regeneration in carbon-aerogel CDI produces no such wastes.

Applications

Processing Radioactive Materials and Wastes. Carbon-aerogel CDI was developed specifically for removing ionic contaminants such as radionuclides and heavy metals from aqueous wastes. With ion exchange, the current standard method used for this purpose, the resulting acid or base secondary waste is itself contaminated, as is the ion-exchange resin when it is eventually replaced. Carbon-aerogel CDI holds the promise of greatly reducing or even eliminating this secondary waste stream in the processing of wastes for the Department of Energy, which holds over a billion gallons



Prototype carbon-aerogel CDI system. Cells containing stacked electrode pairs provide surface area of about 54 acres in a few cubic feet of space.

of sodium nitrate solutions contaminated with radioactive materials. Testing of carbon-aerogel CDI for this application awaits various regulatory approvals.

Commercial and Residential Uses. The most immediately promising uses for carbon-aerogel CDI are as a replacement for the ion-exchange technologies now in use for most commercial and residential applications. The elimination of wastes from chemical regeneration of ion-exchange resins should make carbon-aerogel CDI attractive in both arenas. Homeowners should welcome a water-softening technology that does not require adding rock salt.

Desalination of Brackish Water and Seawater. Desalination of brackish water has been demonstrated, and its energy efficiency makes it attractive almost immediately for this purpose.

Desalination of seawater is equally attractive, but the technology will require further development before this application can be realized.

Recent Work

This system received a U.S. patent in 1994. The major work accomplished on the system in 1994 was the development of a user-friendly automated control system, capable of running carbon-aerogel CDI plants with capacities of hundreds to millions of gallons per day.

Next developmental steps include scaleup (using larger electrodes and larger electrode stacks) to handle greater volumes of water with impurity concentrations of 30,000–40,000 ppm. Our system can now routinely purify water with impurity concentrations of 1000 ppm, and has handled concentrations as high as 10,000 ppm.

We also seek to develop alternatives to the use of ultraviolet light and hydrogen peroxide for oxidative pretreatment of organic contaminants in the feedstream, and to examine the use of chemically generated oxidants against potential organic fouling (including biofouling) of equipment.

Molten-Salt Oxidation of Wastes

An attractive alternative to incineration

Benefits

- Applicable to many kinds of waste
- Fewer products of incomplete oxidation than in other thermal processes
- Reduced risk of radionuclide and toxic metal emission
- Technology is being implemented on the pilot scale

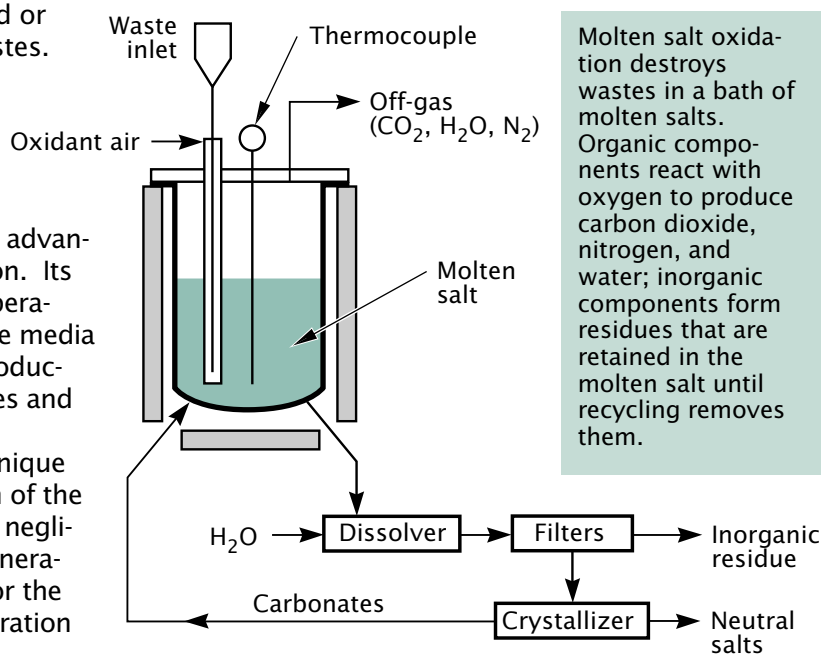
Molten-salt oxidation offers a clean, effective alternative to incineration for the destruction (by oxidation) of hazardous and mixed wastes, medical wastes, chemical warfare agents, and energetic materials such as explosives, propellants, and pyrotechnics. A very stable and controllable technology, it provides in situ scrubbing of acid gases and particulates.

Eliminates Combustion Problems

In molten-salt oxidation (MSO), combustible waste is oxidized in a bath of molten salts (a combination of carbonates of sodium, potassium, and lithium) at 500–950°C. The organic components of the waste react with oxygen to produce carbon dioxide, nitrogen, and water. The inorganic components, including radioactive materials, form inorganic residues that are retained in the molten salt. The salt, being alkaline, “scrubs” any acid gases, such as hydrochloric or sulfuric acid, produced in the oxidation of halogenated or sulfur-containing wastes. Continuous recycling removes residues and neutral salts from the molten salt bath.

MSO offers several advantages over incineration. Its lower operating temperatures and liquid-phase media greatly reduce the production of nitrogen oxides and fugitive emissions of radionuclides. The unique chemistry and design of the MSO process achieve negligible dioxin/furan generation. Also, permits for the construction and operation

of incinerators are difficult to obtain, and public opposition can be strong. Open burning or open detonation of energetic materials is becoming undesirable because of incomplete combustion and the formation of secondary toxic substances, which can lead to degradation of air, soil, and water. The U.S. Army, which has a substantial need for destruction of energetics, has a self-imposed mandate to ban open burning and open detonation by 1997.



Contact:
Martyn Adamson
(510) 423-2024
E-mail: adamson1@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Effective for Many Waste Types

We have been operating MSO reactors since 1991, processing a variety of organic solvents, energetic materials (explosives and/or propellants slurried in oil–water emulsions), and chemical-warfare agent surrogates. We have investigated operation in both single- and two-stage modes, operating the first stage in either a reducing or an oxidizing atmosphere.

While we continue to demonstrate the technology on the bench scale, we are scaling up the processes for destroying both energetic materials and mixed-waste surrogates. A pilot-scale reactor that will process up to 20 kilograms per hour of actual mixed waste is scheduled for demonstration in LLNL's Mixed Waste Management Facility.

Recent Work

LLNL has been investigating the impact of the specific composition of mixed waste surrogates, the operating parameters, and the system design on the process effectiveness. Technical reviews were conducted by DOE in late 1993 and 1994 to assess the state of MSO technology. Using guidance from those reviews, we are investigating four technical issues: minimization of carbon monoxide produced when chlorine is in the waste; the effect of inorganic residue content on the salt melt viscosity; the amount of salt carried into the off-gas lines; and the feasibility of encapsulating the processed salt residue in polyethylene for disposal. These experiments will allow us to determine operating parameters and design systems to minimize salt carryover for the Mixed Waste Management Facility, as well as reach consensus on the best final waste forms for land disposal. These studies will be completed in 1995.

We are seeking industrial partners to develop and commercialize molten-salt systems specially tailored for specific waste streams.

Mediated Electrochemical Oxidation for Treatment of Mixed Waste

A safe, effective alternative to incineration

Benefits

- **Fast, efficient destruction of the organic components of mixed wastes**
- **Inherent process safety: closed-loop systems, with hazardous and radioactive materials contained in an aqueous medium; process works at low temperatures and at atmospheric pressure**

Mediated electrochemical oxidation bench-scale facility equipped with full-scale industrial electrochemical reactor (center). Tests in this facility have achieved 99.99% destruction of cellulosic materials and chlorinated cutting oils.

Large quantities of organic chemicals contaminated with radioactive and hazardous materials are stored throughout the Department of Energy complex awaiting suitable means of disposal. Mediated Electrochemical Oxidation (MEO) can treat these mixed wastes by destroying the organic components and dissolving the radioactive components (even transuranic oxides, which are otherwise difficult to dissolve); the radioactive components can then be recovered or immobilized for disposal. MEO is an aqueous electrochemical process that can destroy a wide variety of organic chemicals by oxidation, converting them into inert materials such as carbon dioxide and water. Almost complete destruction of organics can be achieved at reasonable electrical efficiencies.

Inherently Safe and Widely Applicable

MEO is attractive because it offers a safe and effective alternative to incineration, formerly the most common method for oxidizing organics but no longer acceptable to the public. MEO units are inherently safe for several reasons:

- They operate at moderate temperatures (about 70°C) and at atmospheric pressure.
- They are closed-loop systems, so they present little risk of accidental release into the atmosphere.

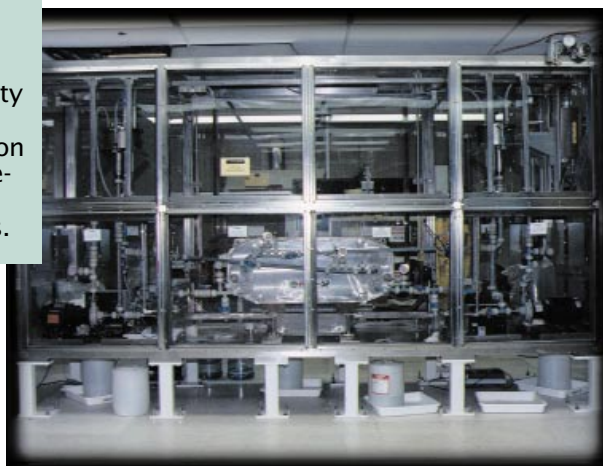
- The hazardous and radioactive materials are contained in an aqueous medium, reducing the risk of accidental release.

MEO is ideally suited for treating liquid and aqueous wastes, but it can also treat slurries, sludges, and finely shredded solid wastes. It can also be used to dissolve and remove surface contamination from equipment and parts, especially those contaminated with mixed wastes. This adaptability gives it potential for widespread and significant application.

Experimental Demonstrations

MEO destroys organic chemicals in an acid solution containing metallic ions, which act as a mediator. The ions, initially in their lower valence state, are oxidized to a higher valence state at an anode. They then destroy organics throughout the bulk of the fluid. We have worked with silver, cobalt, and cerium mediators in nitric and sulfuric acids.

To determine how process parameters affect destruction rates, we conducted many small-scale experiments in laboratory-sized cells. We used two



Contact:
Zohar Chiba
(510) 422-6124
Mail code: L-286
E-mail: chiba1@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

mediator–acid combinations—silver in nitric acid, and cobalt in sulfuric acid—and varied temperature and acid concentration. We generally achieved higher destruction rates at higher temperatures, and with higher acid concentrations, with the more aggressive mediator–acid combination (silver in nitric acid).

Then we carried out experiments at or near optimal conditions in a bench-scale facility using an industrial-scale commercial electrochemical reactor, containing two cell stacks, that can destroy organics continuously (up to half a kilogram an hour). We can directly scale the results of these experiments to a full-sized plant containing many reactors, each containing as many as 60 cell stacks.

In addition to the destruction rates achievable, we are also interested in the destruction efficiency of the MEO process and in the electric-charge (“coulombic”) efficiency, which in part determines the electrical costs of operation. Our work has emphasized reducing cell voltages; we typically operate at less than 2 volts. In general, higher destruction efficiencies require that we pass more current through the system, which reduces the coulombic efficiency. For Trimsol (a chlorinated cutting oil), for example, destruction efficiencies of at least 99% can be achieved at coulombic efficiencies of 70%. Destruction efficiencies of 99.99% can be achieved at coulombic efficiencies of 40–50%.

Recent Work

We recently completed extensive studies of MEO destruction of the major organic components found in combustible mixed wastes stored at DOE's Rocky Flats Plant. We tested Trimsol, cellulose (including paper wipes and cloth), rubber (latex), plastics (Tyvek, polyethylene, and polyvinyl chloride) and biomass (bacteria). (MEO might be used to destroy spent biomass after biodegradation of the organic components of some mixed wastes.) High destruction efficiencies at reasonable coulombic efficiencies were obtained for all of the organics tested except polyvinyl chloride.

We are designing a pilot-scale system to be installed in Lawrence Livermore National Laboratory's Mixed Waste Management Facility, which itself is in the design stage. This system will include the secondary processes (electrolyte regeneration, mediator recovery, and residual waste removal) necessary for continuous operation, and will be integrated with upstream and downstream processes (solid and liquid feed preparation, off-gas and water treatment, and final forms preparation).

Plans are going forward to commercialize MEO for on-site destruction of hazardous organic materials in hospitals and biomedical research institutions, chemical and pharmaceutical companies, university laboratories, and elsewhere. Systems capable of destroying 20–2000 pounds of waste per day are envisaged.

UV/H₂O₂ Treatment of Aqueous Mixed Wastes

Simple, safe, and very clean

Benefits

- Cheaper and easier disposal of aqueous mixed wastes
- Process is simple, safe, and clean
- Allows recycling of treated solutions and water
- Technology is well established

Using a combination of ultraviolet light and hydrogen peroxide (UV/H₂O₂) to remove contaminants from water is a well-established process. We are improving the technology used in current commercial operations to increase its efficiency. The new process will be capable of completely mineralizing the organic constituents of aqueous mixed wastes (waste containing both radioactive and hazardous constituents) and converting them to ordinary radioactive wastes, which will mean cheaper and easier disposal.

A New Application

Under appropriate UV light, hydrogen peroxide undergoes photochemical decomposition, producing strong oxidants that can oxidize many organic compounds to mineralization (that is, carbon atoms are oxidized to carbon dioxide, hydrogen atoms to water, and other non-metallic elements to the corresponding anions). In the improved process, this mineralization is complete.

UV/H₂O₂ treatment has been used in groundwater remediation for years; this project has demonstrated for the first time that it can be used to treat aqueous mixed-waste streams.

Recent Work

We established a Cooperative Research and Development Agreement with an industrial partner in 1993. During 1994 we demonstrated mineralization in organic model compounds (including model contaminants) and completed a comparative study of different kinds of UV lamps.

Organic Model Compounds and Contaminants.

The destruction of oxalic acid (oxalate kill) is necessary in the aqueous processes of plutonium production. We demonstrated that UV/H₂O₂ achieves oxalate kill in hydrochloric acid (HCl) solutions without affecting the HCl concentration. (It is difficult to find a chemical oxidation process that does not affect the chloride ions.) After the

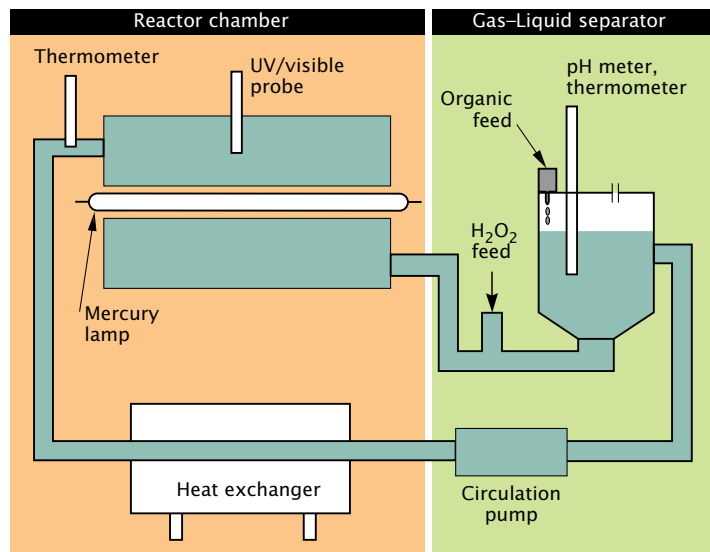


Diagram of the UV/H₂O₂ reactor chamber. Under UV light generated by the mercury lamp, H₂O₂ decomposes to oxidize organic compounds in aqueous mixed waste.

Contact:

Francis Wang
(510) 422-7305
E-mail: wang3@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

oxalate kill, HCl solutions can be reused: the process fulfills the requirement of waste minimization.

In plutonium and uranium production, nitric acid solutions are contaminated with tributylphosphate (TBP) and kerosene. We demonstrated that both TBP and kerosene can be mineralized by the UV/H₂O₂ process.

We applied the process to wastewater streams from Trimsol–water separation (a phase-separation process) and from wet oxidation (which uses H₂O₂ and Fenton's reagents), and the organic constituents were mineralized. In some cases, the treated water can be reused.

During 1995 we will continue to improve the process efficiency and to search for additional target waste streams (generated by DOE/DOD facilities) that can be treated effectively by the UV/H₂O₂ process.

UV Lamps. The choice of UV lamps has an impact on the efficiency and cost of the UV/H₂O₂ process. We compared a mercury lamp and a xenon flashlamp. Preliminary results indicate that for the same input power, the xenon flashlamp produces about twice as many oxidants as the mercury lamp. However, the xenon flashlamp is more complicated to operate and has a shorter lifetime. We will continue studies in 1995 to identify which lamp is a better source of UV light for our purposes.

Excimer lamps are potentially our most effective UV source, and may also have other applications, such as paint stripping. We established a contract to produce at least one excimer lamp with the Institute of High Current Electronics at the Russian Academy of Sciences, where the cost of making excimer lamps is much cheaper than in the U.S.

Flowsheet Development, Modeling, and Systems Analysis for DOE Mixed-Waste Treatment Facilities

Identifying the best options

Benefits

- Coordinated approach to mixed-waste treatment throughout DOE
- Computer simulation of all processes in a fully integrated treatment facility
- Aid to decision makers in evaluating options for treating, transporting, and storing mixed low-level wastes

Coordinated national solutions are needed to solve the problems of treating and disposing of the mixed low-level waste and mixed transuranic waste stored across the Department of Energy (DOE) complex. We are part of a joint effort to develop and analyze alternative flowsheets for operations and processes in mixed-waste treatment facilities, in order to identify options that are technically reasonable, safe, timely, and cost-effective.

Baseline and Two Alternative Flowsheets

This project provides technical support to the DOE Office of Waste Management's Mixed Low-Level Waste Management Program, Applied Technology Program, and Mixed Waste Focus Area. In 1992 and 1993, we led a multi-laboratory team of members from Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Pacific Northwest Laboratory called the Mixed Waste Treatment Project. This group developed a Baseline Flowsheet and two alternative flowsheets for a prototype mixed-waste treatment facility. Each flowsheet contains a fully integrated set of operations and processes to treat a set quantity and distribution of mixed-waste types such as might be assigned to a hypothetical regional DOE treatment facility. A set of functional and operating requirements were developed, and cost and design studies were performed on the Baseline Flowsheet by subcontracted engineering teams led by Los Alamos and Livermore.

Recent Work

We continued technical evaluation of the Baseline Flowsheet and the Nonflame Flowsheet alternative in 1994. We joined with Los Alamos and an industrial partner to perform computer simulations of the Baseline Flowsheet using software called ASPEN. The ASPEN models include realistic unit operations with thermodynamic and chemical data, and they simulate all processes in a fully integrated treatment facility with interconnected treatment trains and recycle streams. As a result, ASPEN is now available for use, and can be used to evaluate alternative generic flowsheets, site-specific flowsheets, and flowsheets for implementing Federal Facility Compliance Agreements.

For the Nonflame Flowsheet, we commissioned and guided an extended design study. In this study, nonthermal processes operating below 350°C were used as alternatives to incineration and other thermal treatment. Technologies that were examined included separation of organics from the waste matrices by soil washing, sludge washing, and debris

Contact:
Richard Ragaini
(510) 423-8877
E-mail: rragaini@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

washing with aqueous solutions and solvents, followed by low-temperature destruction of the removed organics. Specific commercial processes were selected, process flow diagrams were modified, and material balances for these systems and flowsheet were calculated. The conclusion of the study was that the Nonflame Flowsheet was viable for DOE waste streams, and worthy of more detailed study.

The Office of Waste Management also requested us to perform a peer review of the analytical methodology used in a report on systems analysis of mixed low-level waste treatment. This systems analysis methodology is an analytical tool that will aid decision makers in evaluating the feasibility and effectiveness of various management options for mixed low-level waste, and in choosing the best option for implementation. These options consist of various plans for treating, transporting, and storing mixed low-level wastes from DOE facilities across the country. The review assessed the correctness of the procedures used and the adequacy of the methodology for the intended purpose.

Risk and Hazards Analyses of Mixed-Waste Treatment Technologies

Initial steps toward Final Safety Analysis Reports

Benefits

- Aids technology design
- Identifies potential hazards for safety-system design

Department of Energy (DOE) orders and regulations require risk and hazard analyses of proposed DOE nuclear facilities; these analyses are important because they aid in technology design efforts and identify potential hazards for design of safety systems. We performed risk and hazard analyses of mixed-waste treatment technologies proposed for use in the Mixed Waste Integrated Program.

Assessing Potential Hazardous Conditions

The Mixed Waste Integrated Program was part of the DOE Environmental Management's Office of Technology Development. Its mission was to develop and demonstrate innovative technologies for the treatment and management of DOE's mixed low-level wastes. The program's vision was that DOE will choose technologies that improve final waste-form performance, reduce risks during waste treatment, and minimize costs. Emerging technologies will be selected on the basis of three criteria:

1. Systems analyses that are founded on sound technical bases.
2. High public acceptance.
3. Regulatory acceptance.

The initial step in a risk assessment is a Preliminary Hazards Analysis (PHA), which is a qualitative assessment of the potential hazardous conditions associated with elements of a waste treatment system. A PHA establishes an initial hazard categorization for a DOE nuclear facility using the technologies and identifies processes and structures that may affect or be important to safety.

The PHA is followed by a Preliminary Safety Analysis Report (PSAR), prepared during Title I and II design. The PSAR leads to preparation of the Final Safety Analysis Report, which is prepared during construction, testing, and acceptance and is completed before routine operation begins.

Recent Work

We completed PHAs for two technologies in this project in 1994: the plasma hearth process and vitrification by joule heating. The plasma hearth PHA was based on the plasma hearth pilot plant being demonstrated in Ukiah, California. The vitrification PHA was based on the joule melting technologies being demonstrated at the Clemson University Industrial Center for Vitrification Research.

The methodology employed in these analyses was a step-by-step identification of potential hazards involved in the handling, characterization, and treatment of mixed waste by the two processes. We evaluated hazards related to hazardous and radioactive materials inventory, fire, accidental releases, natural phenomena (for example, earthquakes), natural gas, process explosions, electrical systems, and other industrial activities.

Contact:

Richard Ragaini
(510) 423-8877
E-mail: rragaini@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Hazardous-materials and radiological assessments were carried out independently. The conclusion of the hazardous-materials assessment was that facilities using either process would have minimal on-site and off-site impacts on the public or the environment, and would therefore be "Low-Hazard." With respect to radioactive materials, the facilities would be either Exempt (that is, non-nuclear),

Category 3, or Category 2, depending on the maximum inventory of radioactive materials selected. The calculations indicate that there would be no significant impact to off-site personnel or the environment. Other competing mixed-waste treatment technologies that require larger inventories of hazardous and/or radioactive materials would have higher potential impacts than either vitrification or the plasma hearth process.

The California Environmental Enterprise

Advancing land reuse and environmental technology development

Benefits

- **Cooperative action to facilitate economic reuse of environmentally impaired sites**
- **Development, demonstration, validation, and commercialization of innovative environmental technologies**
- **Consultation on technology brokering**

Remediation of contaminated land is often delayed because businesses have a high perceived risk in obtaining the regulatory approvals and the best cleanup technologies. The primary mission of the California Environmental Enterprise (CEE) is to reduce the financial risk of site owners, lenders, and developers and to increase the economic value of selected sites. CEE is a technology-services network of national laboratories, state agencies, private industry, and universities working together to facilitate the economic and rehabilitative reuse of environmentally impaired properties.

Seeking Novel Solutions

In cooperation with federal agencies, CEE works with the private sector to seek novel technological solutions to environmental-restoration and waste-management problems at sites needing cleanup. Through the development of public-private partnerships, CEE brokers private-sector solutions and helps commercialize environmental technologies. CEE is a joint project of Lawrence Livermore National Laboratory, Lawrence Berkeley Laboratory, and Sandia National Laboratories-California in conjunction with the California Environmental Protection Agency (Cal/EPA).

CEE's Principal Activities

Technology Demonstration.

Demonstrating new cleanup technologies at designated Cal/EPA "Walk-In Program" cleanup sites.

Technology Validation. Helping Cal/EPA validate technologies from environmental technology firms that apply to the AB 2060 Technology Certification Program.

Technology Brokering and Commercialization. Implementing a system that matches public and private customers and suppliers to facilitate the development and commercialization of environmental technologies.

Technology Training. Improving education and training to meet the needs of environmental stakeholders through such activities as:

- Training and facilitation workshops for owners of contaminated properties.
- Management workshops for startup environmental technology companies.
- Regionalized public/private training programs to facilitate land reuse.

Contact:
Richard Ragaini
(510) 423-8877
E-mail: rragaini@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Information Management. Developing (with Cal/EPA) a clearinghouse to meet the information needs of environmental stakeholders through activities such as:

- “Environmentally contaminated California real estate” information system.
- “Hotline” information services.
- Newsletter.

Recent Work

CEE collaborated with Cal/EPA and the Institute of Environmental Solutions (IES) on a “Walk-In Program” cleanup project at a former cannery site on the San Joaquin River in Antioch, California, where the soil is contaminated with cyanides and

heavy metals. IES had already broken the cleanup gridlock that existed at the Antioch site by facilitating interactions between the site owner, the City of Antioch, the State Water Board, the State Department of Toxics, other financial stakeholders, and public interest groups.

In conjunction with an industrial partner and the State of California, Lawrence Livermore National Laboratory demonstrated a field-portable gas-chromatograph/mass spectrometer that can measure groundwater contamination at the Antioch site to parts per billion. Lawrence Berkeley Laboratory advised on constructing a wetland there to remediate the heavy-metals contamination.

Using High-Performance Computing to Evaluate the Effectiveness of Aquifer Remediation

A more realistic way to predict the behavior of groundwater contamination under active remediation

Benefits

- Contaminant-migration problems can be studied on a very detailed, geostatistical basis
- Subsurface heterogeneity can be represented realistically
- Remediation options can be studied from the perspective of probabilistic risk assessment

Computer simulation of fluid flow and chemical migration in subsurface aquifers is routinely used to study the processes associated with cleaning up groundwater contamination. The accuracy of these simulations can be hampered by the lack of information describing properties and structure of subsurface formations, by the way in which the available data are used, and, in some cases, by the size of the problem itself. To provide more reliable insight into how effective subsurface remediation technologies are, we are combining more powerful computer-simulation techniques with traditional forms of data in a new way. This approach provides a better representation of the kind of behavior we see in natural systems.

Problem: the Subsurface is Nonuniform

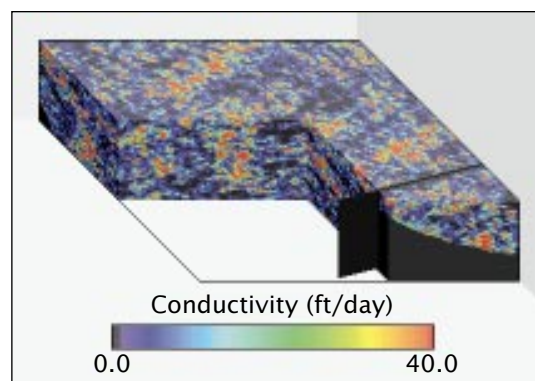
In most subsurface environments, rock, soil materials and the material properties that affect groundwater flow are distributed in a complex and nonuniform fashion. In practical problems, the existence of this heterogeneity is usually revealed in the well measurements that are available to characterize an aquifer. Since the number of measurements is typically small compared with the total area, a full, detailed description of the aquifer seems impossible to make.

The normal approach, therefore, has been to use representative average values to construct a simple “bulk” description of the system. However, there is increasing concern about the influence of aquifer heterogeneity on groundwater flow and contaminant transport, and about whether it is adequately represented in this type of simple model. Failure to recognize or incorporate the effects of small-scale process interactions in field-scale models could lead to unreliable conclusions about system behavior, especially when they are used to design and understand cleanup procedures.

The ParFlow Model

We designed a model called ParFlow to simulate extremely large, detailed, and three-dimensional groundwater flow problems, so that if such detailed descriptions of heterogeneous aquifer properties were available, cleanup problems could be more reliably represented and understood. ParFlow requires a significant degree of computational power—it is designed for implementation on massively parallel supercomputers such as the Cray T3D at Lawrence Livermore National Laboratory (LLNL).

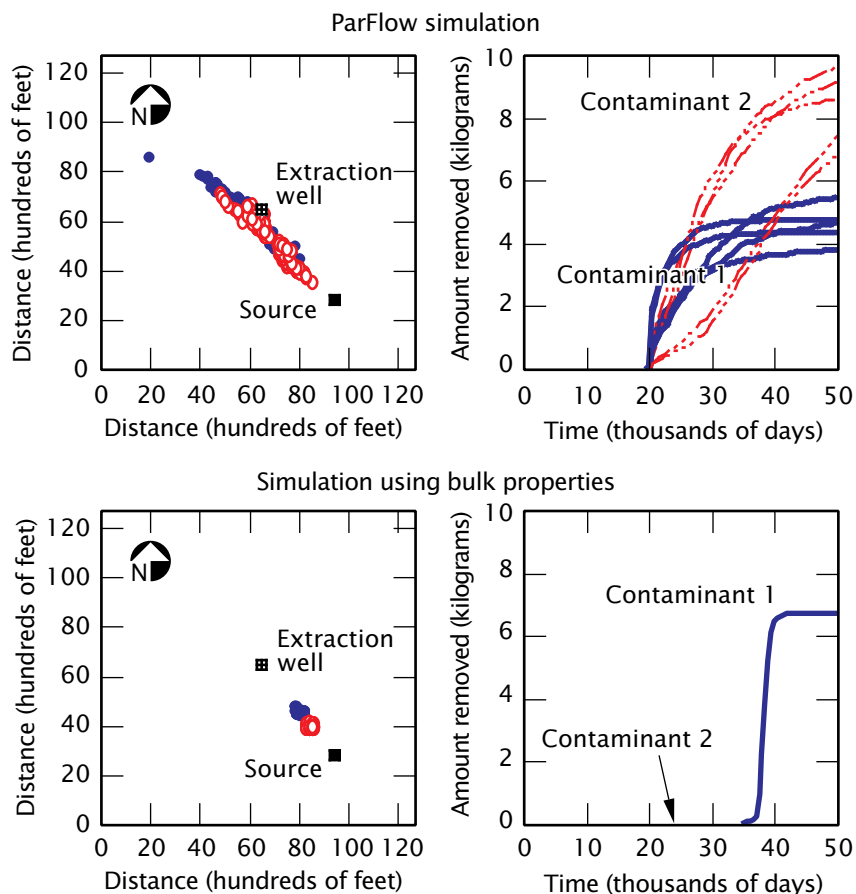
One ParFlow “realization” of the hydraulic conductivity in the test aquifer. The flow of water through soil is directly proportional to the conductivity. The region is roughly 12,700 feet square and 320 feet deep; lower clay and fault zones are evident.



Contact:
Andrew Tompson
(510) 422-6348
E-mail: afbt@llnl.gov

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Contrast between ParFlow simulation and conventional bulk-properties simulation: (left) bird's-eye view of the spatial distribution of two contaminants 20,000 days after release; (right) amount of contaminant removed after an extraction well is turned on at 20,000 days.



Recent Work

We began testing ParFlow in 1994 to simulate groundwater flow and migration of dissolved contaminants using the geological features of the water-bearing aquifer directly beneath LLNL. It was contaminated decades ago with several organic compounds; efforts are now under way to remove the chemicals by pumping out the groundwater and removing the chemicals on the surface. Our results show how different interpretations of the available data can develop distinctly different predictions of future contaminant migration and recovery.

Heterogeneity and Structural Features.

Instead of assigning a constant “bulk” property to an aquifer layer, our approach allows heterogeneity to be represented statistically on a detailed level. Statistical “realizations” of the aquifer system properties were constructed to reproduce patterns of heterogeneity inferred from the regularly available data, while retaining larger, well-known structural features of the system. In the LLNL problem, these features include a continuous, impermeable lower clay layer, a fault zone, and an alluvium layer composed of various amounts of sands, silts, clays, and gravels.

Contaminant Migration. Using several realizations, we ran an equivalent number of simulations to predict the migration of two contaminants placed near the water table to the north of the fault. The contaminants were allowed to move northwest with the ambient groundwater flow for 20,000 days (55 years), after which a central extraction well was turned on and allowed to remove the contaminants by drawing nearby groundwater out for the next 30,000 days (to 137 years after the release). Because of chemical reactions, the contaminants move at slightly different rates. These problems were designed to answer questions such as “How effective is the rate of extraction? How much does heterogeneity affect the progress of extraction? How realistic are the results?”

In one group of problems, we used five statistically identical realizations of the aquifer properties to define the system. The statistics were derived from a single set of 200 property measurements. Because of heterogeneity, the contaminants were shown to be heavily dispersed in the direction of flow, as is commonly observed at contaminated sites. In general, removal of contaminant 2 in these problems took longer, but was more complete than removal of contaminant 1 because contaminant 1 moves faster and much of it had migrated past the well before pumping was initiated.

Differences in the sets of results arise from the separate property realizations and their specific impact on the migration. Although the “real” result cannot be determined in a single simulation, the distribution of results can be used to estimate the expected recovery in a statistical sense. This allows analysis of problems from the perspective of probabilistic risk assessment.

In contrast, another problem that used a single “bulk” property to describe the aquifer—the average of the same 200 measurements—showed no significant dispersion of the contaminants. Instead, they appeared as confined pulses, moving somewhat slower than in the problems that incorporated heterogeneity. The removal of contaminant 1 was more sudden and complete, but occurred at a later time. The removal of contaminant 2 was so slow that it was not observed in the time frame of the simulation.

These problems demonstrate that more realistic and reliable results are obtained when heterogeneity is statistically reproduced and the power of the ParFlow model is exploited. Future work will include addition of more accurate conditions representing this particular site, as well as applications to problems at other locations.

Modeling Pore-Scale Processes in Porous Media

More physically realistic models help our understanding of fluid flow and chemical reactions in porous soils

Benefits

- The interdependence of interfacial area, pressure, and saturation in multiphase flow in porous media can be evaluated
- Theoretical predictions of average flow and diffusive and reactive behavior can be linked with bulk observations in real systems

Fluid flow and chemical reaction phenomena in porous systems have important applications in problems in groundwater flow, agricultural irrigation, petroleum reservoir engineering, and chemical engineering. Normally, mathematical descriptions of these processes are expressed at levels that are large enough to be observed with the naked eye—that is, at a macroscopic, or continuum, level of observation. Although many of these models have been successfully applied in practice, their utility may be restricted because of our limited knowledge of the fundamental physics involved. To improve our understanding of these systems, we are developing more physically realistic continuum-scale models of multiphase flow and chemical diffusion and reaction in porous media.

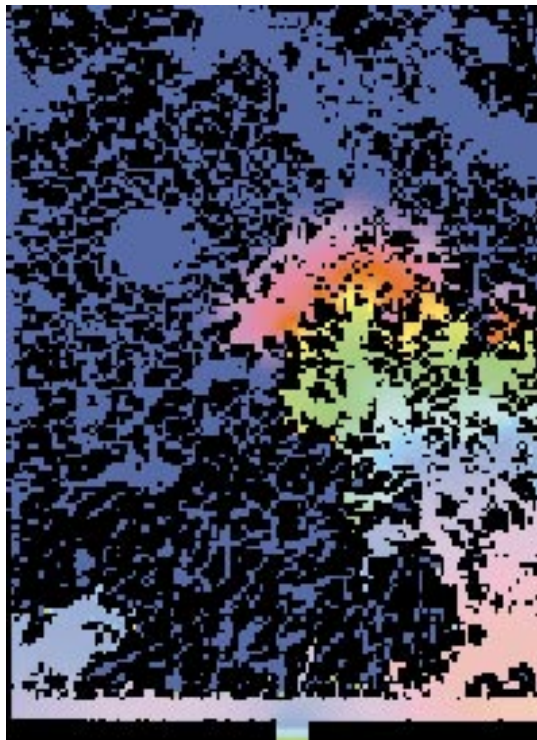
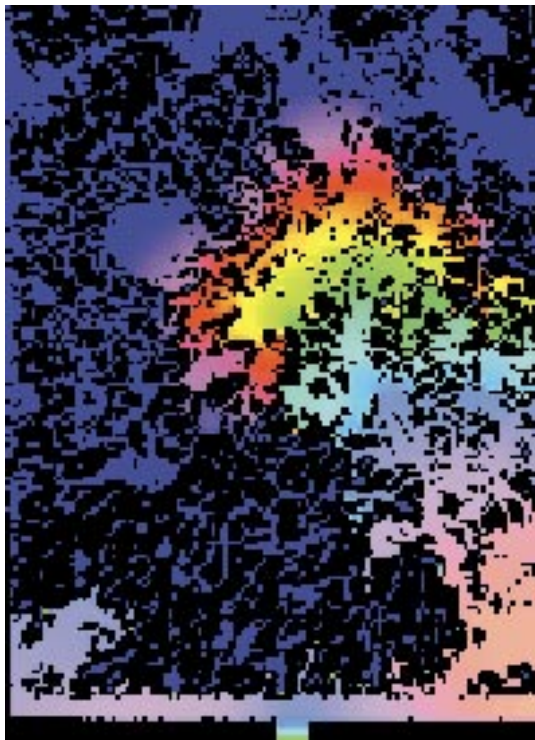
Simulating Processes in the Pores

In continuum-scale descriptions, the mathematical terms used are quantities that have been averaged over representative bulk volumes of the medium, such as the average water flux through a soil column or the mean aqueous chemical concentration within a volume of soil. This approach is used because of the disparity in scales: it is impossible to observe intricate pore networks or otherwise measure complicated grain geometries. Hence, bulk models of flow and reaction phenomena have been developed from gross balance concepts (such as mass and momentum) and from approximate relationships that were formulated by observing experiments.

Improving these models requires careful theoretical and experimental analyses. Our approach is to conduct experiments based on simulation of flow, transport, and reaction processes in the pores themselves and then to scale up the results to the macroscopic level. These simulations will complement analogous theoretical analyses and physical experiments, and help to improve the continuum-scale models.

Multiphase Flow. Traditional descriptions of flow in unsaturated (multiphase) soil are based on an extension of Darcy's law: the fluid flow rate in a saturated soil is proportional to the soil permeability and the local fluid pressure gradient. In unsaturated soil, multiple fluid phases simultaneously occupy and move through the pore spaces. The average flow rate of each phase is usually considered to be proportional to a relative permeability, which depends on the relative saturation of that phase, and to a pressure gradient that is based on the average pressure in each phase. Typically, relationships between permeability, saturation, and pressure must be measured experimentally for the models to be used in practice.

The fundamental understanding of this model has many limitations. It fails to fully account for how microscopic surface-tension phenomena between multiple fluids and solid surfaces affect the relationship between average pressure and saturation. Surface-tension effects are usually represented in experiments by an average pressure difference between two coexisting phases in a soil. This capillary pressure is commonly



Two snapshots (digitized, two-dimensional slices) of a simulation of solute distribution at the pore scale: here, in carbonate with an intricate, fluid-saturated pore structure. A non-reactive chemical tracer is added (left) to establish a baseline distribution of concentration. Then a simple chemical reaction is enforced at the grain boundary between the solute and the solid minerals (right), and the resulting solute distribution is determined. In this example, the chemical reaction retards the solute distribution. (Courtesy Los Alamos National Laboratory.)

related to phase saturations. However, measurements show that the capillary pressure in a system has a hysteretic (nonunique) behavior; that is, the instantaneous state of pressure in the system may be affected by the history of the saturation in an experiment—for example, whether conditions were wetting or drying. Therefore, this state of pressure may depend on more than just saturation. Also, the macroscopic capillary pressure measured in unsaturated air–water systems is often reported to be very large, so large that it cannot be explained by the possible pressures that may exist in water and air. In other words, as used and measured in practice, capillary pressures represent a state of energy (as embedded phase interfaces) in the system in addition to the real pressure state. However, this state of energy is never rigorously incorporated into the model or the experimental method.

An improved theory has been proposed to more fully represent these effects. The theory systematically averages interfacial tension effects along the way to incorporate the effects of multiphase interfacial phenomena. Initial results indicate, for example, that the macroscopic capillary

pressure may depend not only on the bulk saturation but also on the average interfacial area between two phases in a unit volume of soil. This finding suggests that the history of saturation, or the state of interfacial energy, may be reflected in the interfacial area in the system—a quantity that may differ between wetting and drying conditions.

Recently, a new experimental technique was developed to measure the fluid saturation and interfacial area in an actual porous medium over a series of static equilibrium configurations. This technique should allow for interfacial areas, pressures, and saturations to be measured at the pore scale so that their interdependence can be determined at the macroscopic level. We are pursuing a similar upscaling approach with a numerical Lattice–Boltzmann model, in conjunction with Los Alamos National Laboratory. Ultimately, we will incorporate the measured relationships of capillary pressure, saturation, and interfacial area into traditional models of multiphase flow, along with improved relationships of permeability and saturation and an equation to predict the migration of interphase surface area with the basic flows.

Chemical Migration and Reaction.

Traditional descriptions of chemical migration and reaction in porous media use diffusion laws to describe the bulk effects of molecular diffusion and hydrodynamic dispersion. These descriptions frequently borrow traditional laboratory (beaker-scale) reaction formulations and representations without accounting for the structure and presence of the porous medium. On a microscopic level, the abundance of chemical species may vary from one pore location to another, depending on the local flow and diffusion conditions, the proximity of reactive mineral surfaces, the stoichiometric balance conditions implied by local reaction relationships, and the overall distribution of constituents in the system. At the macroscopic level, the laws governing reactions may not necessarily parallel those studied in the beaker and may instead depend on the medium's composition, structure, and flow characteristics.

Recent Work

Because bulk, nondestructive reaction experiments in porous media are difficult to execute, our approach is to simulate the flow, transport, and reaction processes in the pores themselves and

integrate, or scale up, the numerical results to the macroscopic level. In 1994 we performed simulations using soil elements with various pore structures. First, flow is induced through a system, and a nonreactive chemical tracer is added to establish a baseline distribution of concentration. Then a simple chemical reaction is enforced at the grain boundary between the solute and the solid minerals, and the resulting solute distribution is determined. The corresponding macroscopic description of the reaction is expressed in terms of cross-sectionally averaged concentrations, a measure of average mineral abundance, and a factor that accounts for the kinetics of reaction at the macroscale as affected by the geometric structure of the medium.

Similarly, the bulk laws describing diffusion and dispersion at the macroscopic level must be modified to account for the porous medium, especially when modeling reactive constituents. In fact, dispersion is an artifact of working with averages; it is not a process defined at the pore scale. We believe that pore-scale simulations or pore-scale physical experiments can be used to link theoretical predictions of average flow and diffusive behavior with bulk observations in real systems.

Environmental Technologies Program Publications, FY 1994

- Andricevic, R., J. I. Daniels, and R. L. Jacobson (1994), *Radionuclide Migration Using Travel Time Transport Approach and Its Application in Risk Analysis*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-116584; presented at Desert Research Institute (Las Vegas, NV) and submitted to *J. Hydrol.*
- Angel, S. M., T. Vess, K. Langry, K. Kyle, and T. Kulp (1993), "Development of Remote Sensing Methods for Environmental and Process Monitoring Applications," in *Proc. Electrochemical Soc., Chemical Sensors II* **P93-7**, p. 625.
- Ashby, S. F., W. J. Bosl, R. D. Falgout, S. G. Smith, A. F. B. Tompson, and T. J. Williams (1994), "A Numerical Simulation of Groundwater Flow and Contaminant Transport on the Cray T3D and C90 Supercomputers," *Proc. 34th Cray User Group Conf.* (Tours, France: October 10–14, 1994); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-118635.
- Ashby, S. F., R. D. Falgout, S. G. Smith, and T. W. Fogwell (1994), "Multigrid Preconditioned Conjugate Gradients for the Numerical Simulation of Groundwater Flow on the Cray T3D," in *Proc. Am. Nucl. Soc. Int. Conf. Mathematics and Computations, Reactor Physics, and Environmental Analyses* (Portland OR: April 30–May 4, 1995); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-118622.
- Ashby, S. F., R. D. Falgout, S. G. Smith, and A. F. B. Tompson (1993), "Modeling Groundwater Flow on MPPs," in *Proc. 1993 Scalable Parallel Libraries Conf.* (Mississippi State University, October 6–8, 1993); also Lawrence Livermore National Laboratory, Livermore CA, UCRL-JC-115602.
- Ashby, S. F., R. D. Falgout, S. G. Smith, and A. F. B. Tompson (1994), "The Parallel Performance of a Groundwater Flow Code on the Cray T3D," in *Proc. Seventh SIAM Conf. Parallel Processing for Scientific Computing* (San Francisco, CA: February 15–17, 1995); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-118604.
- Bergman, W., G. Larsen, R. Lopez, K. Wilson, K. Simon, and L. Frye (1994), "Preliminary Field Evaluation of a High Efficiency Steel Filter," in *Proc. 23rd DOE/NRC Nuclear Air Cleaning Conf.* (Buffalo, NY); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-115893.
- Bergman, W., G. Larsen, F. Weber, P. Wilson, R. Lopez, K. Wilson, P. Moore, C. Gellner, D. Rapchun, K. Simon, J. Turley, L. Frye, and D. Monroe (1993), "Development and Evaluation of a Cleanable High Efficiency Steel Filter," in *Proc. 22nd DOE/NRC Nuclear Air Cleaning Conf.*, CONF-9020823, pp. 586-614; also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-109769.
- Bergman, W., K. Wilson, G. Larsen, and R. Lopez (1993), "Aerosol Filtration with Steel Fiber Filters," in *Proc. Am. Filtration Soc. Annual Meeting*; also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-113854.
- Camp, D. C., J. Pickering, and H. E. Martz (1994), "Design and Construction of a 208-L Drum Containing Representative LLNL Transuranic and Low-Level Wastes," in *Proc. Nondestructive Assay and Nondestructive Examination Waste Characterization Conf.* (Pocatello, ID: February 14–16, 1994); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-115672.

- Chiba, Z., P. R. Lewis, and L. C. Murguia (1994), "Mediated Electrochemical Oxidation Treatment for Rocky Flats Combustible Low-Level Mixed Waste," in *Final Report to Rocky Flats Plant, FY 1993 and 1994*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-118679.
- Daniels, J. I., Ed. (1993), *Pilot Study Risk Assessment for Selected Problems at the Nevada Test Site (NTS)*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-LR-113891.
- Daniels, J. I., R. Andricevic, L. R. Anspaugh, and R. L. Jacobson (1993), *Risk-Based Screening Analysis of Ground Water Contaminated by Radionuclides Introduced at the Nevada Test Site (NTS)*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-112789.
- Daniels, J. I., R. Andricevic, R. L. Jacobson, and L. R. Anspaugh (1993), *Accounting for Predictive Uncertainty in a Risk Analysis Focusing on Radiological Contamination of Ground Water*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-110903 ABS; presented at Int. Conf. Groundwater Quality Management (Tallinn, Estonia: September 6–9, 1993).
- Dietsche, L. J., R. S. Upadhye, J. A. Pendergrass, D. C. Camp, T. K. Thompson, and L. C. Borduin (1994), *ASPEN Computer Simulations of the Mixed Waste Treatment Project Baseline Flowsheet*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-118122.
- Dougherty, D. E. (1994), "Building Groundwater Optimizers That Respond to the Needs of Decision-Makers," in *Proc. Annual Water Resources, Planning and Management Conf.* (Denver, CO: May 1994).
- Ebbinghaus, B. B., O. H. Krikorian, and M. G. Adamson (1994) "Vaporization of Actinide Oxides in Thermal Treatment Processes for Mixed Waste," in *Proc. Symp. Thermodynamic Applications in Materials Processing* (Rosemont, IL: October 2–6, 1994); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-116414.
- Hamilton, L. D., S. Holtzman, A. Meinhold, S. C. Morris, R. Pardi, C. Sun, J. I. Daniels, D. Layton, T. E. McKone, and T. Straume (1993), *Pilot Study Risk Assessment for Selected Problems at the Savannah River Site (SRS)*, Brookhaven National Laboratory, Upton, NY, BNL-48776.
- Hamilton, L. D., A. F. Meinhold, S. L. Baxter, S. Holtzman, S. C. Morris, R. Pardi, M. D. Rowe, and C. Sun (1993), *Pilot Study Risk Assessment for Selected Problems at the Fernald Environmental Management Project (FEMP)*, Brookhaven National Laboratory, Upton, NY, BNL-48777.
- Hamilton, L. D., A. F. Meinhold, S. L. Baxter, S. Holtzman, S. C. Morris, R. Pardi, M. D. Rowe, C. Sun, L. R. Anspaugh, K. T. Bogen, J. I. Daniels, D. W. Layton, T. E. McKone, T. Straume, R. Andricevic, and R. L. Jacobson (1994), "Pilot Study Risk Assessment for Selected Problems at Three US Department of Energy Facilities," *Environ. Int.* **20**(5), 585–604; also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-118416.
- Hamilton, L. D., A. F. Meinhold, S. L. Baxter, S. C. Morris, R. S. Holtzman, S. C. Morris, M. D. Rowe, J. I. Daniels, D. W. Layton, and L. R. Anspaugh (1994), *Lessons Learned: Needs for Improving Human Health Risk Assessment at US DOE Sites*, Brookhaven National Laboratory, Upton, NY, BNL-60157.
- Janecky, D. R., and A. F. B. Tompson (1994), "Diffusion Calculations in Detailed Pore Scale Models for Transport Coupled to Chemical Reactions," *EOS, Trans. Am. Geophys. Un.* **75**(44), 207.
- Layton, D. W., L. R. Anspaugh, K. T. Bogen, and T. Straume (1993), *Risk Assessment of Soil-Based Exposures to Plutonium at Experimental Sites Located on the Nevada Test Site and Adjoining Areas*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-112789.
- Martz, H. E., D. J. Schneberk, and G. P. Roberson (1994), "Real-Time Radiography, Digital Radiography, and Computed Tomography for Nonintrusive Waste Drum Characterization," in *Proc. Nondestructive Assay and Nondestructive Examination Waste Characterization Conf.* (Pocatello, ID: February 14–16, 1994); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-115670.
- Martz, H. E., D. J. Schneberk, and G. P. Roberson (1993), "Three-Dimensional Nonintrusive Imaging of Obscured Objects by X-Ray and Gamma-Ray Computed Tomography," in *Proc. Underground and Obscured Object Imaging and Detection* (Orlando, FL: April 15–16, 1993), Vol. 1942, pp. 236–249; also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-113474.

- McGrath, W. A., and G. F. Pinder (1994), "Delineating a Contaminant Plume Boundary," in *Proc. 10th Int. Conf. Computational Methods in Water Resources* (Heidelberg, Germany: Kluwer Academic Press).
- Moore, P., W. Bergman, and H. Gilbert (1993) "Survey of Life-Cycle Costs of Glass-Paper HEPA Filters," in *Proc. 22nd DOE/NRC Nuclear Air Cleaning Conf.*, CONF-9020823, pp. 849-862.
- Nitao, J. J., and G. A. Bear (1994), *Potentials and Their Roles in Transport in Porous Media*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-111741; submitted to *Water Resources Research*.
- Ragaini, R. C., M. Aycok, D. Coordes, J. Russell, W. TenBrook, and P. Yimbo (1993), *Preliminary Hazards Analysis—Plasma Hearth Process*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-CR-116222; also DOE/MWIP-13.
- Ragaini, R. C., M. Aycok, and J. Russell (1993), "Risk Assessments of Innovative Technologies for Treatment of Mixed Waste," in *Risk Assessment Methodology Applied to D&D and Environmental Restoration—II*, *Trans. Am. Nucl. Soc.* Vol. 69; also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-115800.
- Ragaini, R. C., D. Coordes, M. Ruggieri, J. Russell, W. TenBrook, and P. Yimbo (1994), *Preliminary Hazards Analysis—Verification Processes*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-CR-116576; also DOE/MWIP-27.
- Ragaini, R. C., and James E. Russell (1994), "Technology Risk Assessments for Mixed Waste Integrated Program," Mid-Year Review Presentation, April 19, 1994, Washington, DC.
- Ramirez, A. L., and W. D. Daily (in press), "Electrical Resistance Tomography During In Situ TCE Remediation at the Savannah River Site," *J. Appl. Geophys.*; also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-112326.
- Ramirez, A. L., and W. D. Daily (1993), *Monitoring Radio-Frequency Heating of Contaminated Soils Using Electrical Resistance Tomography*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-115373.
- Ramirez, A. L., and W. D. Daily (1994), *Monitoring Six-Phase Ohmic Heating of Contaminated Soils Using Electrical Resistance Tomography*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-118418.
- Rashidi, M., L. Peurrung, A. F. B. Tompson, and T. J. Kulp (1994), *Experimental Analysis of Pore-Scale Flow and Transport in Porous Media*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-116520.
- Richards, J., S. Brown, F. Milanovich, B. Healey, S. Chadha, and D. Walt (1995), *Development of the Indicator-Photopolymer Chemistries for Multianalyte Sensor Arrays*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-120404.
- Roberson, G. P., H. E. Martz, D. J. Deckman, D. C. Camp, S. G. Azevedo, and E. R. Keto (1994), "Characterization of Waste Drums Using Nonintrusive Active and Passive Computed Tomography," in *Proc. Nondestructive Assay and Nondestructive Examination Waste Characterization Conf.* (Pocatello, ID: February 14-16, 1994); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-118317.
- Tompson, A. F. B., S. F. Ashby, R. D. Falgout, and S. G. Smith (1993), *On the Role of High Performance Computing for Simulating Subsurface Flow and Chemical Migration*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-114179.
- Tompson, A. F. B., S. F. Ashby, R. D. Falgout, S. G. Smith, T. W. Fogwell, and G. A. Loosmore (1994), "Use of High-Performance Computing to Examine the Effectiveness of Aquifer Remediation," in A. Peters, G. Wittum, B. Herrling, U. Meissner, C. Brebbia, W. Gray, and G. Pinder, Eds., *Computational Methods in Water Resources X*, Vol. 2 (Dordrecht: Kluwer Academic Publishers); also Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-115374.

Technical Information Department
Lawrence Livermore National Laboratory
University Of California
Livermore, CA 94551